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APPLICATION OF WILLGERODT-KINDLER REACTION FOR SYNTHESIS OF DIACIDS AND POLYMERS THEIR FROM

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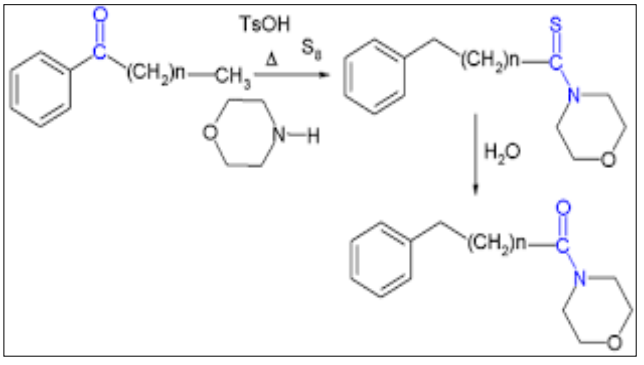
ABSTRACT :

Aromatic polymers have been widely used in aerospace, electrical and electronic application because of their outstanding thermal stability mechanical strength at elevated temperature and electrical properties[]. The high temperature resistant polymers have different types or classes like aromatic polyamides, polyimides, polybenzimidazoles, polyquinoxalines polyhydrazides. However technological application of most of thesepolymera are limited processing difficulties because of high melting or glass transition temperature (Tg) and poor solubility in the most of common organic solvents due to rigid backbones and strong interchain interactions. Many attempt were made to synthesis soluble polyamides, polyimides by incorporation of bulky pendant group or cardio groups [2-5]. Flexible linkages and polar groups [8-9] Theses modification lower the melting temperature and lead to soluble and amorphous polymers without any significant reduction of thermal stability.

KEY WORDS:*Aromatic polymers , aerospace, electrical and electronic application.*



INTRODUCTION:

Co-polymerization has been regarded as an effective method for modificaing the chemical structure of polymers to improve their processability [10]. Much effort has been made to develop structurally modified aromatic polyamides, polyimides, such as poly(amide-imide)s [15-17] polyesterimides, the polymers incorporateed with flexible linkages like $–CH_2$-, -O-, -S-, -SO-, SCl_2-. The two different functionalities with flexible $–CH_2$ –group in single polymer shows improved polymers which are processable.

One of approach is made to prepare diacid containing di-imide along with flexible methylene group. For introduction of flexible methylene several methods are used, Here our approach is by using Willgerodt Kindler reaction the flexible methylene group in introduced in acids. Such a diacid is used to prepare polyamides with different diamines.

SYNTHESIS OF BIFUCTIONAL MONOMERS

Experimental Methods

The following commercially available chemicals were used as received. Pyromelliticdian hydride (PMDA), benzophenonetetracarboxyldianhydride(BTDA) 3/4 amino acetophenone ,DMAc ,pyridine ,benzene, toluene, acetic anhydride .

A)Synthesis of diacids

I.Bis N N'-4 caboxyl phenyl, 1,2,4,5 phenylenediimide (I)

The diacid synthesized from PMDA/BTDA and 4-amino-acetophenone. The reaction was perfomed in two steps. In the first step amic acid synthesis and in second step cyclisation amic acid to imide was made. In a 500 ml three neck round bottle flask equipped with a magnetic stirrer a thermeowell and condenser, 5 gm (0.0229 mole) of PMDA was placed under the flow of

nitrogen. To this 50 ml of N N dimethyl acetamide was added. The temperature of mixture is maintaining 0-5Oc. A semisolid mixture is formed. To the mixture 6 gm (0.0444 mole) of 4-amino acetophenone was added. This mixture is stirred at 0-5^{0}C for 2 hr. The ice bath is removed and the reaction mixture was stirred at room temperature for 3 ,hrs. The reaction mixture was poured in icecold water. The solid separates, is washed with cold water and dried at room temperature i.e. in sunlight. The yield of product is 8 gm

C=69.0%, H=3.54%, O= 21.24%, N = 6.19 %.

II. Bis N, N p-phenyl 4-thioacetomorphelide

In 500 ml round bottom flask equipped with reflux condenser, magnetic stirrer were placed 22.6 gm (0.05 mole) (I), 4.6 gm (0.05 mole) sulphur and 13.05 g (13 ml 0.15 mole) morpholine. The resulting reaction mixture was stirred suitably under gentle reflux until the evolution of hydrogen sulphide subsides and more vigorously for 14 hr. The reaction mixture was allowed to cool and 200 ml ethanol was added, to obtain buff coloured product which was filter, washed with excess of ethanol and dried.

Yield of product 84 %
C= 62.39 %, H=4.59 % O= 14.68 %, S= 9.79 %, N=8.56%.

III. Bis N, N p-phenyl 4-,4' Dicaboxylic acid

In one litre round bottom flask equipped with reflux condenser, magnetic stirrer were placed. 32.7 (0.05 mole) (II) and 500 ml 10 % ethanolic sodium hydroxide solution. The reaction mixture was refluxed with stirring for 12 hr. The most of the ethanol was distilled out under reduced pressure To the residual product 500 ml hot water was added and filtered. The filtrate was acidified by 1:1 hydrochloric acid. The precipitated product was filtered, washed thoroughly with hot water and dried. The product was recrystallized from ethanol to get white pure methylene di acid (II).

C= 64.46 %, H=3.30 %,O= 26.45% %, N=5.79 %

SYNTHESIS OF POLYMERS

A 100 mL three neck round bottom flask was equipped with magnetic stirrer, nitrogen gas inlet , calcium chloride guard tube ,thermowell. 2,5-Bis (4-aminophenyl) 3,4 - diphenyl thiophine 0.418g (0.001 mol) and novel diacid (0.001) 0.452g by direct polycondensation method using Yamazaki's phosphorylation method. Triphenyl phophite was used as acondensing agent, where in mixture of NMP and pyridine (4:1 vol) conting 8% anhydrous Lithum Chloride was employed as solvent.The polymerization were carriedout at 100OC for 3 h. The different aromatic diamines used for sysnthesis of polymers.

Table 1: % Yield, Inherent viscosity of Polyamide

Sr. NO.	Polymer Code	mol % Diacid	mol %		Yield (%)	η_{inh} [b] (dL/g)
			ODA	TPTDA		
1	PA-1	100	100	00	89.4	0.56
2	PA-2	100	75	25	98.4	046
3	PA-3	100	50	50	91.6	036
4	PA-4	100	25	75	90.5	0.53
5	PA-5	100	00	100	91.1	0.43

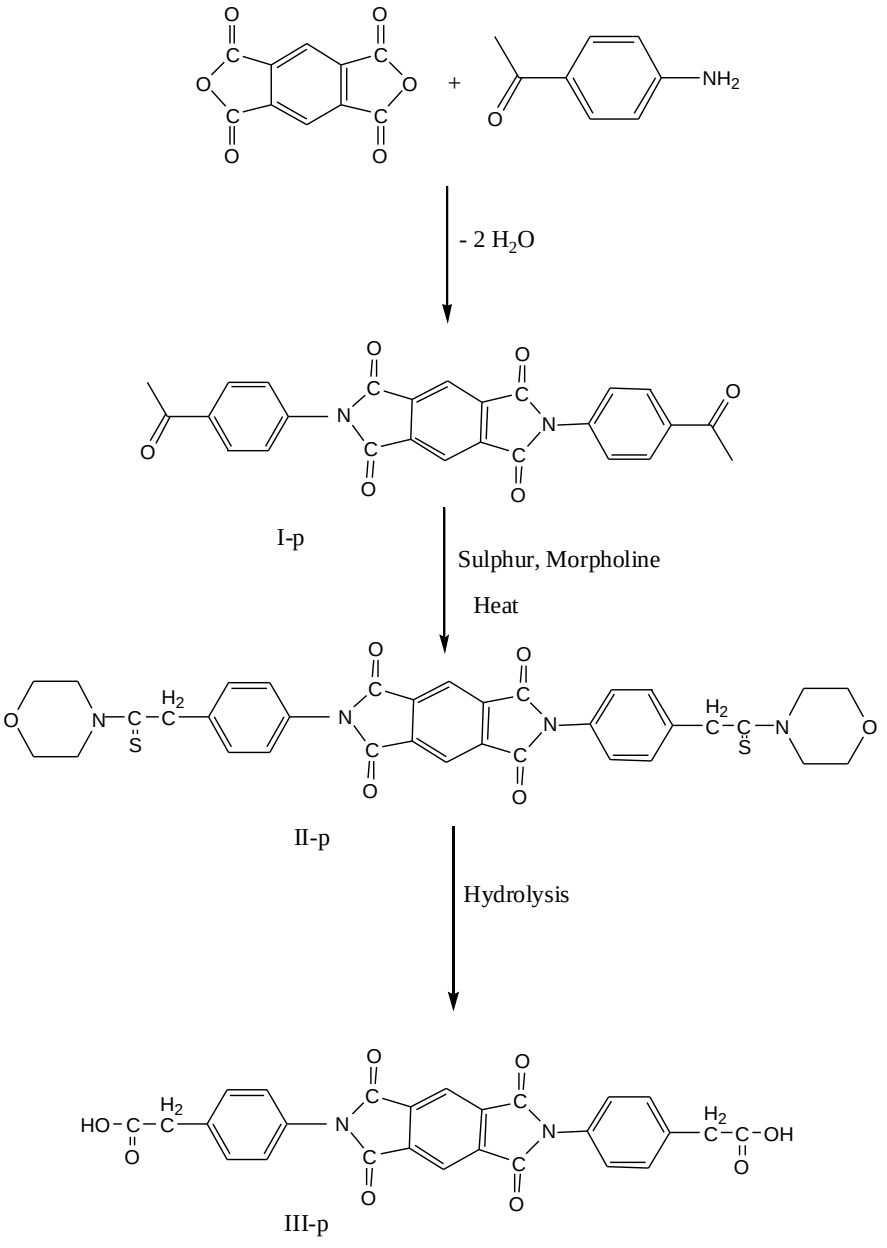
Table 2: Thermal analysis of Polyamide

Sr. NO.	Polymer Code	Ti[b] (℃)	Tmax[c] (°C)	Residual wt. at 900 ℃ (%)
1	PA-1	375	430	17.0
2	PA-2	340	417	16.9
3	PA_3	380	421	10.7
4	PA-4	328	433	10.12
5	PA-5	374	449	22.3

Table 3: Solubility of Polyamides

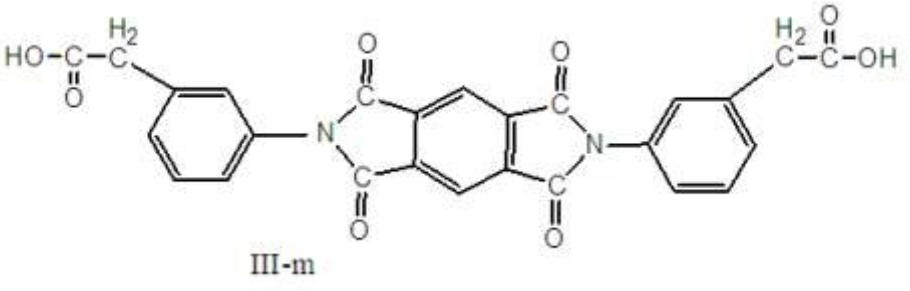
POLYMER→ / SOLVENT ↓	PA-1	PA-2	PA-3	PA-4	PA-5
TCE+phenol	++	++	++	++	++
DMAc	++	++	++	++	++
NMP	++	++	++	++	++
DMSO	++	++	++	++	++
THF	--	--	--	--	--
m- Cresol	++	++	++	++	++
Pyridine	++	++	++	++	++
THF	--	--	--	--	--
DCM	--	--	--	--	--
Chloroform	--	--	--	--	--
Acetone	--	--	--	--	--
Conc. H_2SO_4	++	++	++	++	++

++ = Soluble at room temperature
+ = Soluble on heating
+- = Partly soluble
- = Insoluble



Scheme I: Synthesis of diimide containing diacid III-p and III-m.

Similarly scheme can be run with m-aminoacetophenone to give III-m analogues to III-p



SCHEME I: Synthesis of diimide containing diacid III-p and III-m.

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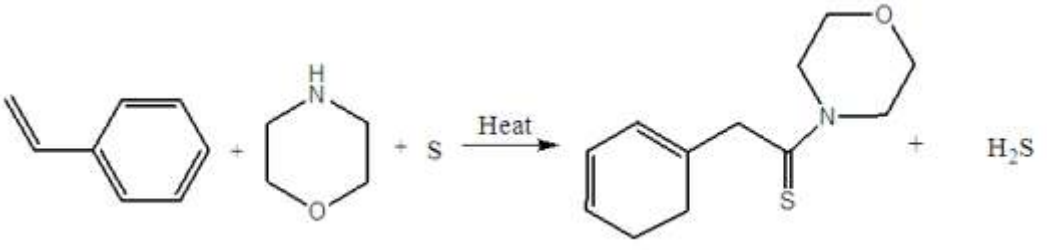
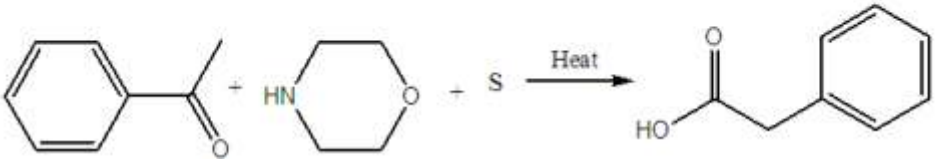
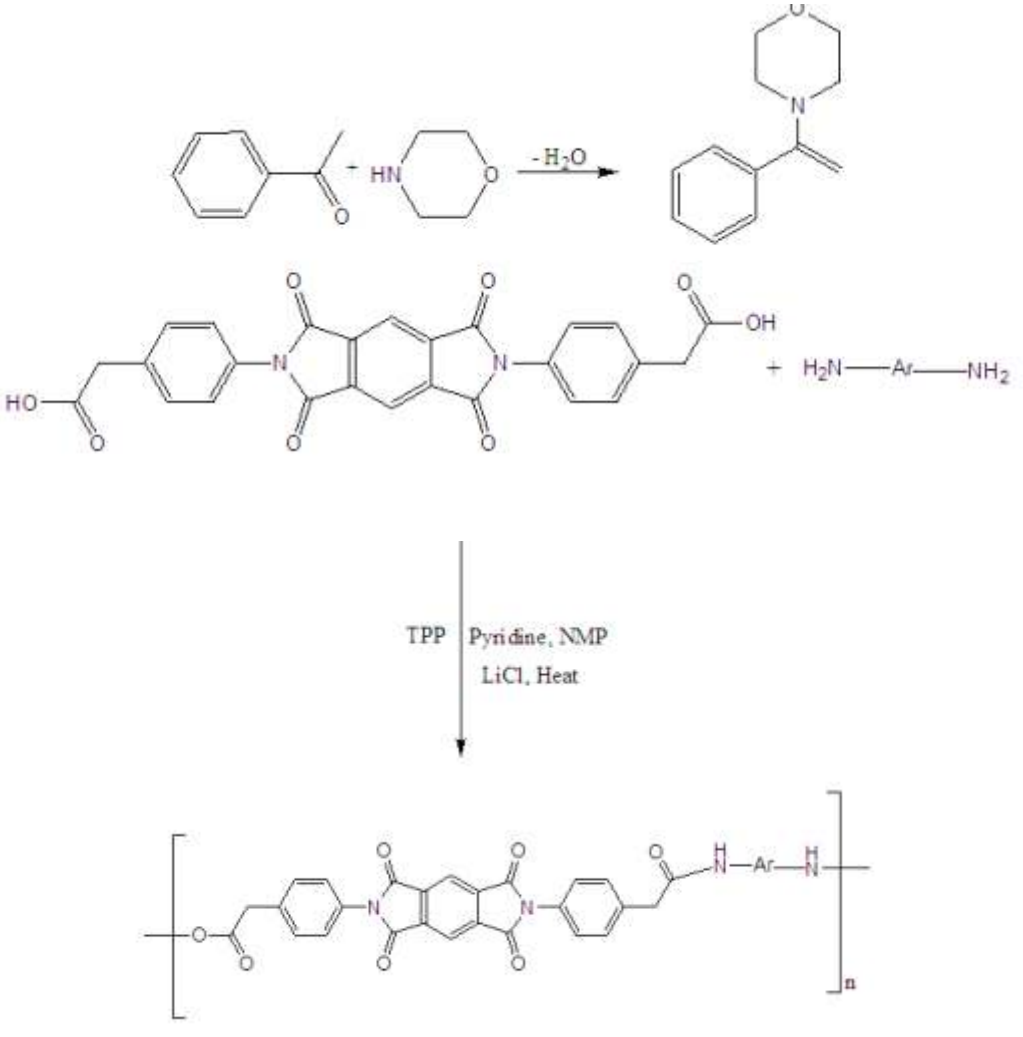
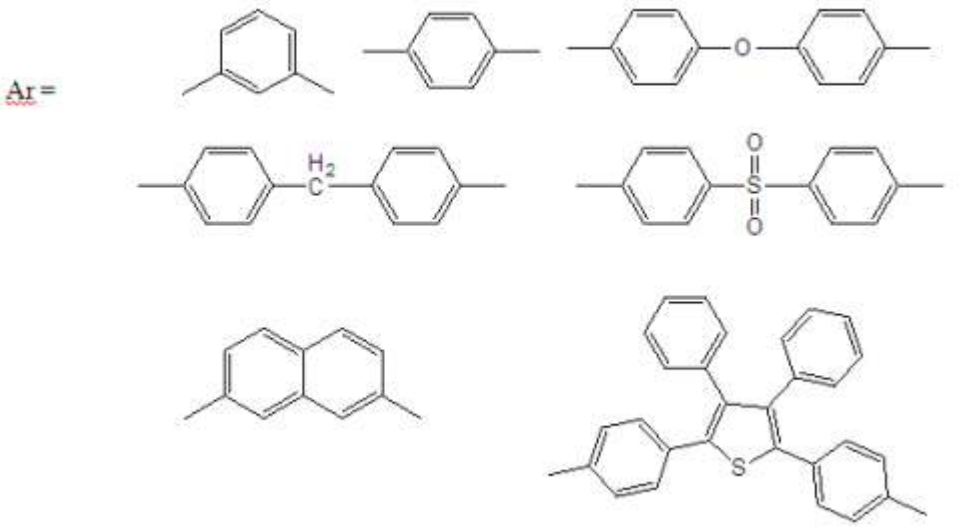
Synthesis of model reaction of Diacid





Mechanism:





SCHEMEII: Synthesis of poly(amide-imide)s from III-p / III-m

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