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PREPARATION AND CHARACTERIZATION OF NOVEL KETO-ETHER - HYDRAZIDE BASED ON APPLICATION OF POLYMER SYNTHESIS

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ABSTRACT

Synthesis of a new monomer was having flexible keto-ether linkages which are the essential criteria for the process ability of polymer. A new dihyrazide i.e. bis 4 (4 -benzoyl phenoxy) benzoic acid hydrazide (BPBH) was synthesized by using p-hydroxy benzhydrazide with 4, 4´-diflourobenzophenone in the presence of K_2CO_3 as a dehydrating agent by azeotropic distillation. Synthesized monomer was characterized by FT-IR, NMR spectroscopic techniques. Dihydrazide was soluble in polar aprotic solvent.

KEYWORDS

Hydrazide, Azeotropic distillation and Polar aprotic solvent.

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INTRODUCTON

Hydrazides are a class of organic compounds sharing a common functional group characterized by a nitrogen to nitrogen covalent bond with 4 substituents with at least one of them being an acyl group. The general structure for a hydrazide is E (=O)-NR-NR_2, where the R's are frequently hydrogens[1-4]. Hydrazides can be further classified by atom attached to the oxygen: carbohydrazides (R-C (=O)-NH-NH_2), sulfonohydrazides (R-S $(=O)_2$-NH-NH_2) Hydrazide moiety not only applicable in drug synthesis but also wide application in polymer synthesis[5-6]. The process ability is of prime importance for heat resistant polymers[7]. The characteristics that contribute to the thermal stability also make it more difficult to process, namely poor solubility and high melt temperatures[8-11]. Considering the potential applications of polymers, synthesis of new organic aromatic monomers with special functionalities is greatly needed to fine-tune polymers for specific tasks[12]. There are approaches to improve process ability of high performance / high temperature polymers by making use of structurally modified, substituted functional organic aromatic monomers[13-18]. The prime objective of the present research was to improve process ability /solubility of thermally stable polymers namely These monomers containing a flexible ether linkage, preformed amide linkage and heterocyclic moiety were expected to provide the structural characteristics required for the improvement of thermal stability and process ability[19,20].

EXPERIMENTAL

MATERIALS

Terephthalic acid, isophthalic acid, (80%) hydazine hydrate, N-methyl pyrrolidone, pyridine, dimethyl sulphoxide, methanol, lithium chloride were purified and dried. Lithium carbonate (S. d. fine) was vacuum dried at 100ºC for 6 h hexamethyl phospharamamide (HMPA) was purified by refluxing and fractional distillation. It was stored over Linde type 4A molecular sieves**.** P-hydroxybenzoic acid, 4, 4´- diflourobenzophenone were (S.d. fine) used after purification.

Following materials were purified by the standard methods as given below

1. Methanol (S.d. fine Chem. Ltd. Mumbai) was dried with calcium hydride and distilled. It was stored over Linde type 4A molecular sieves.
2. Terephthalic acid and isophthalic acid (Aldrich chemical) were purified by sublimation under reduced pressure.
3. P-hydroxy benzoic acid was recrystallised from ethanol.
4. Isophthalyol chloride and terepththylyol chloride were purified by recrystallisation in dry hexanol.

Characterization

IR spectra were recorded at a resolution of 4 cm^{-1} with co-addition of 32 scans using a Thermo-scientific Nicolet iS10 smart IR. ^{1}HNMR spectra were recorded with a Bruker 400 MHz and 100 MHz for ^{13}C measurements using $CDCl_3$ or DMSO solvent

Monomer synthesis

Synthesis of dimethyl isophthalate (DMI)

In a 2 litre three neck round bottom flask, equipped with overhead mechanical stirrer, dropping funnel, reflux condenser were placed 100 g (0.6 mol) isophthalic acid and 300mL methanol 80 mL concentrated sulphuric acid was added slowly through dropping funnel with stirring and ice water cooling. The reaction mixture was gently refluxed for 8 h. The excess methanol was distilled and finally under vaccum. The residual solid was transferred to 1 litre water in a beaker and excess of acid was neutralized by sodium hydrogen carbonate. The reddish oil (ester) separated with 200mL chloroform; extract washed twice with water and stored over anhydrous sodium sulphate. Sodium sulphate was removed by filtration, chloroform was distilled off. The residual ester was distilled under vacuum at 120ºC/2mm.

Yield 85g (73%)

M.P. 68-69ºC (Lit. M.P. 68-71ºC)

Synthesis of isopthaloyl dihydrazide (IDH)

In 1 litre round bottom flask, 50 g (0.25mol) dimethyl isophthalate, 200mL methanol and 60mL hydrazine hydrate (80%) were placed. The reaction mixture was refluxed for 8 h. The excess hydrazine hydrate and methanol was distilled off under vacuum. The isophthalyol dihydrazide was recrystallised from distilled water.

Yield 40g (80%)

M.P. 234ºC (Lit. M.P. 224-231ºC)

Synthesis of terephthalyol dihydrazide (TDH)

Terephthalyol dihydrazide (TDH) was synthesised from terephthalic acid by following the similar procedure.

Yield 42g (82%)

M.P. >300ºC

Synthesis of isophthaloyl chloride (IPC)

In a 500mL round bottom flask equipped with reflux condenser , calcium chloride guard tube , magnetic stirrer were placed 35 g (0.21mol) isophthalic acid (IPA), 75mL thionyl chloride and 3mL pyridine. The reaction mixture was heated to gentle reflux for 6 h. The excess thionyl chloride was distilled off azeotropically using dry benzene. It was purified by distillation under vacuum and recrystallised from dry hexane.

Yield 40 g (94%)

M.P. 41ºC (Lit- M.P. 43-45ºC)

Synthesis of terephthaloyl chloride (TPC)

In a 500mL round bottom flask equipped with reflux condenser calcium chloride guard tube, magnetic stirrer were placed 35 g (0.21mol) terephthalic acid 75mL thionyl chloride and 3mL pyridine. The reaction mixture was refluxed till all acid dissolved. The excess thionyl chloride was removed and the residual acid chloride was purified by distillation under vacuum and recrystallised distilled product from dry hexane.

Yield 039.8 g (93.36 %)

M.P. 81-82ºC (Lit. M.P.:-80-82ºC)

Synthesis of p -hydroxybenzoic acid methyl ester (pHBE)

In a 1 liter three necked round bottom flask, equipped with magnetic stirrer, dropping funnel, reflux condenser were placed 40g (0.2894mol) p-hydroxybenzoic acid and 500mL methanol. 10mL sulphuric acid was added slowly through dropping funnel with stirring and ice water cooling. Reaction mixture was refluxed for 8 h. Excess methanol was distilled off and final traces were removed under vacuum. The residual acid salt of methyl ester was dissolved in 100mL methanol and carefully neutralized by sodium hydrogen carbonate. A white colored precipitate was obtained. It was filtered and purified by distilling under vacuum.

Yield: 32g (80%)

M.P. 126ºC (Lit. M.P.128 ºC)

Synthesis of p-hydroxy benzhydrazide (pHBH)

In 1 liter three neck round bottom flask equipped with magnetic stirrer, calcium chloride guard tube, reflux condenser were placed 30 g (0.197mmol) methyl-phydroxy benzoate (pHBE), 80mL methanol and 10mL hydrazine hydrate (80%). The reaction mixture was refluxed for 2 h with stirring. The excess methanol and hydrazine hydrate was distilled off under vacuum. The product p-hydroxy benzhydrazide was recrystallized from chloroform.

Yield: 21 g (70%)

M.P. 264ºC (Lit.M.P. 264-265ºC)

Synthesis of bis 4(4 -benzoyl phenoxy) benzoic acid hydrazide (BPBH) (IX)

To a 250mL three neck round bottom flask equipped with a magnetic stirrer, a Dean-stark trap, nitrogen inlet, thermo well and a condenser, 0.657g (0.00435mmol) (pHBH), 1.89 g (0.0087mmol) 4, 4´-diflourobenzophenone and 1.19g (0.0087mmol) K_2CO_3 were added. To this mixture 20mL DMAc and 40mL dry distilled toluene was added. The reaction mixture was stirred under nitrogen and refluxed at 125ºC for 18 h azeotropically to remove water. The reaction temperature was slowly raised to 160ºC over a period of 4 h to remove water and continued for 3 h at 160^{o}C.The reaction mixture was then cooled to and product was precipitated by pouring in ice-cold water. The dihydrazide was stirred in water at 60ºC. It was filtered and then stirred in methanol for 4 h at 50ºC. Resulting dihydrazide was filtered and dried under vacuum at 70ºC for 8 h.

Yield 0.28 g (60%)

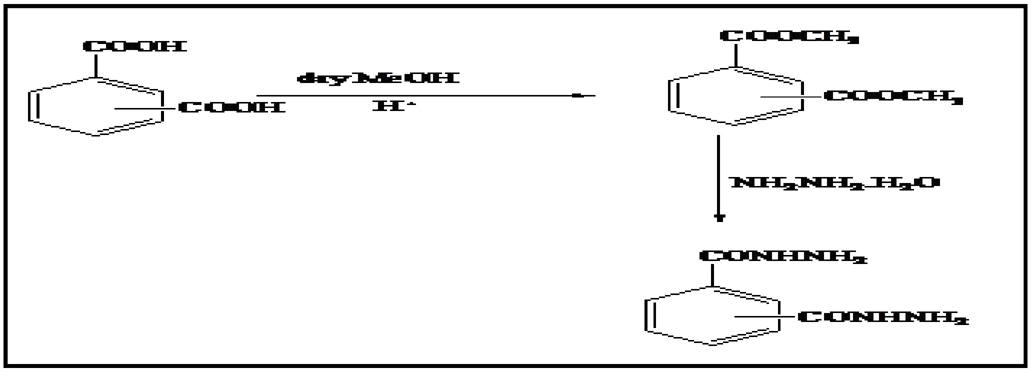
M.P. >300ºC

Table No.1: Solubility data of dihydrazide

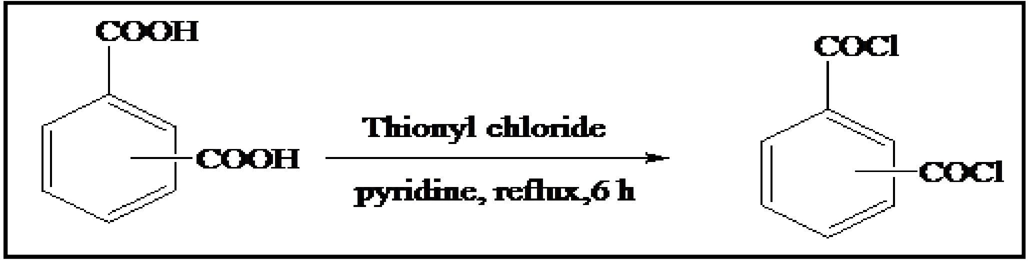
S.No	Solvent	
1	DMAc	++
2	DMSO	++
3	NMP	++
4	DMF	++
5	Pyridine	++
6	m-cresol	+-
7	Conc.H_2SO_4	++
8	Nitrobenzene	-
9	DCM	-
10	Chloroform	-
11	EtOH	-

Table No.2: Spectroscopic data of dihydrazide

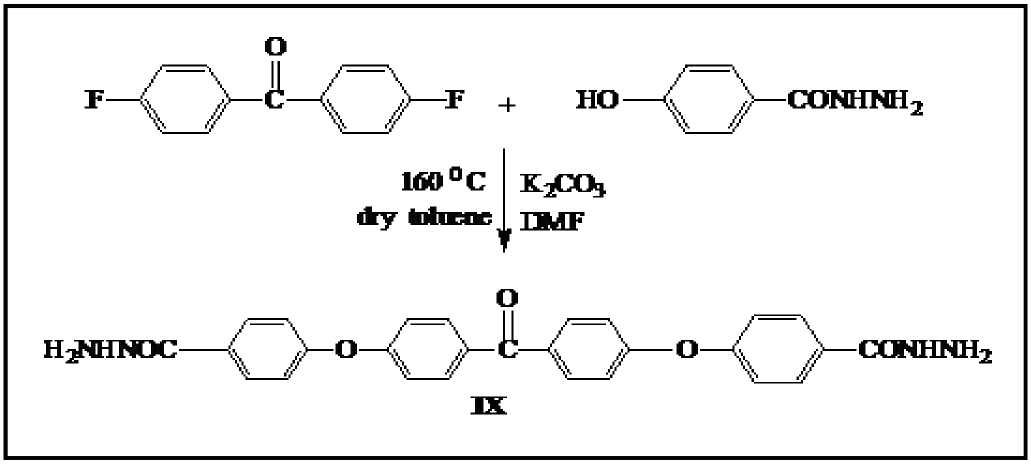
S.No	Spectroscopy	Stretching frequency	Analysis
1	IR	1724 cm^{-1}	C-O-C stretch
		1629 cm^{-1}	C=O stretch in amide
		3167, 3071 cm^{-1}	-NH stretching
2	^{1}HNMR	4.6 ppm	-NH_2 absorption
		8.6 ppm	-NH in amide
		7.16-7.48 ppm	para substituted benzene
3	^{13}CNMR	178 ppm	-C=O absorption peak of ketone
4	Mass	482.9 m/e	Molecular ion peak
		452 m/e	Base peak due to loss of NH_2 group
		423 m/e	Loss of –$CONHNH_2$



Scheme No.1: Synthesis of isophthalic acid dihydrazide (IDH) and terephthalic acid dihydrazide (TDH)



Scheme No.2: Synthesis of isophthalyol (IPC) and terephthalyol chloride (TPC)



Scheme No.3: Synthesis of bis 4 (4- benzoyl phenoxy) benzoic acid hydrazide (BPBAH)

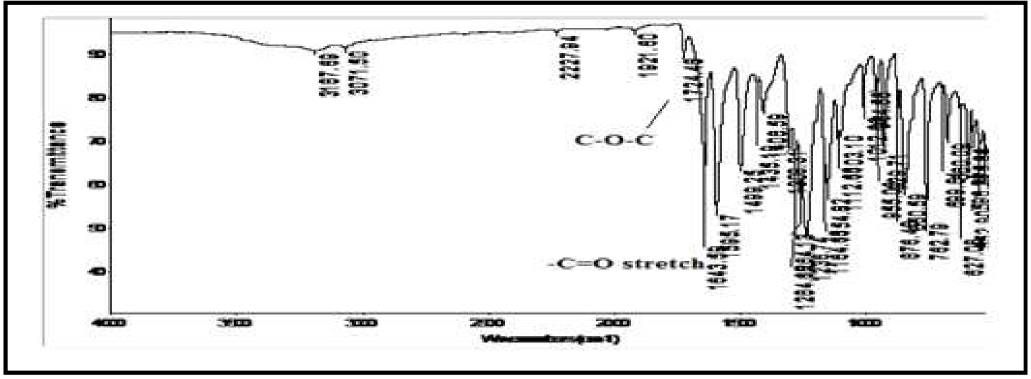


Figure No.1: IR Spectra of monomer BPBAH

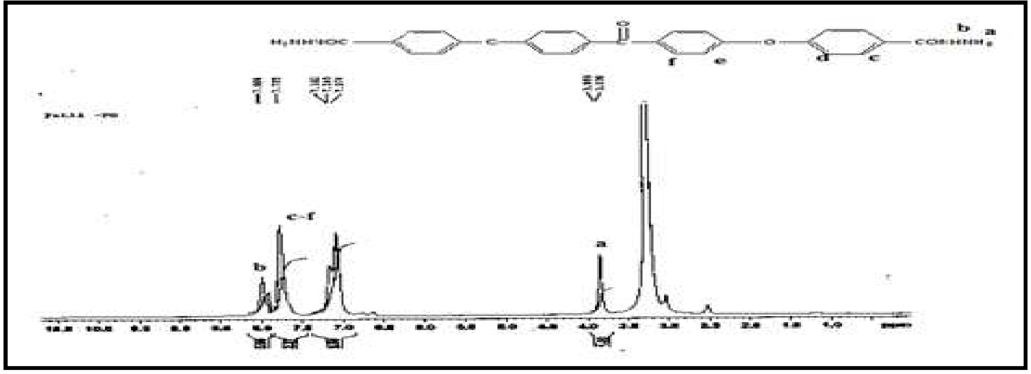


Figure No.2: ^{1}HNMR Spectra of monomer BPBAH

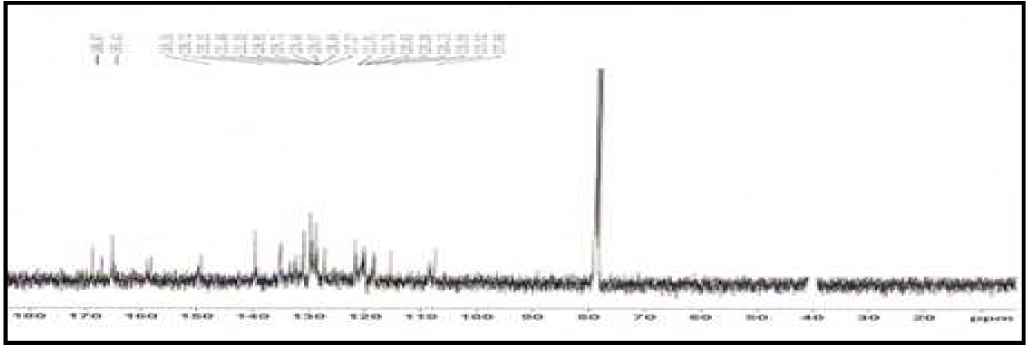


Figure No.3: ^{13}CNMR of BPBAH

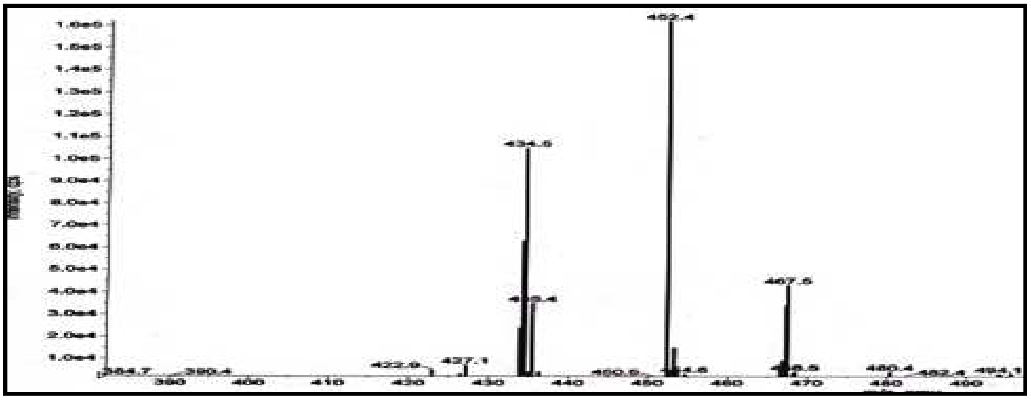


Figure No.4: Mass spectra monomer

CONCLUSION

Synthesized new monomer i.e. dihydrazide having the flexible keto ether linkages shows the solubility in polar aprotic solvent. In this work we try to modify the monomer for the purpose of preparation of high performance processable polymer.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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