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ORIGINAL ARTICLE

SYNTHESIS AND CHARACTERIZATION OF S- TRIAZINE CONTAINING POLYAZOMETHINES WITH NAPHTHOXY PENDENT GROUP

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ABSTRACT:-

A series of s-triazine containing polyazomethines containing naphthoxy pendent groups were synthesized from newly synthesized dialdehydes containing s-triazine ring with diamines namely p-phenylene diamine (PPD) and m-phenylene diamine (MPD) in m-cresol by solution polycondensation technique. The resulting polyazomethines were characterized by FT-IR spectroscopy, inherent viscosity, solubility tests, thermogravimetric analysis and X-ray diffraction studies.

KEYWORDS:-*2, 4-bis (4-formylphenoxy) 6-α/β-naphthoxys-triazine [4/3FP(β)NT]s-triazine, polyazo - methines, Solutionpolycondensation.*

INTRODUCTION

Aromatic polyazomethines are thermally stable, film forming and fiber forming materials and exhibit good mechanical strength. Generally, they are insoluble in organic solvents. To overcome this difficulty, several attempts have been made in the past to synthesize soluble and high molecular weight polyazomethines by incorporation of sulfone groups [1, 2] in the polymer chain and methyl, methoxy, alkoxy and halogen substituents on the benzene ring. [6-9] The introduction of heterocyclic groups in the polymer backbone is another approach to improve the solubility and thermal stability of polyazomethines.[2, 5, 10, 11] The introduction of s-triazine ring and ether groups in the polymer backbone has been demonstrated to improve the solubility of polyazomethines.[12]

In the present investigation, polyazomethines were synthesized from newly synthesized dialdehydes containing s-triazine ring with commercially available diamines namely p-phenylene diamine (PPD), m-phenyleneand diamine (MPD) in m-cresol by solution polycondensation technique. The resulting polyazomethines were characterized by FT-IR spectroscopy, inherent viscosity, solubility tests, thermogravimetric analysis and X-ray diffraction studies.

EXPERIMENTAL

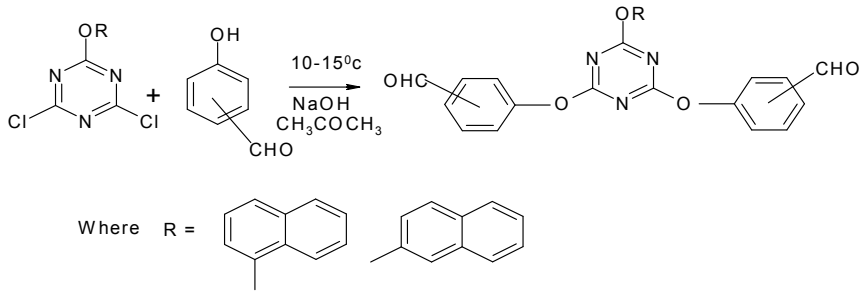
Material

p-Phenylene diamine (PPD) and m-phenylene diamine (MPD) (Colligens) were purified by sublimation under vacuum. Cyanuric chloride was recrystallized from petroleum ether. Methanol and m-cresol were purified by distillation prior to use.

Synthesis of s-triazine containing dialdehydes.

Dialdehyde monomers containing s-triazine ring were synthesized by the route shown in **Scheme-1** The cyanuric chloride derivatives namely 2,4-dichloro-6-α-naphthoxy-s-triazine and 2,4-dichloro-6-β-naphthoxy-s-triazine readily underwent nucleophilic displacement of chloride ions by phenolate anion formed from p-/m-hydroxy benzaldehyde to yield the corresponding dialdehydes

3FP(β)NT, 4FP(β)NT, 3FP(α)NT, and 4FP(α)NT. All aldehydes were obtained in good yields. The physical characteristics are given in **Table-1**



Scheme-1 Synthesis of s-triazine containing dialdehydes

Table-1 Physical characteristics of s-triazine containing dialdehydes

Dialdehyde	Yield (%)	M.P (°C)	Elemental Analysis	C	H	N	M^+
4FP(β)NT	99	163-165	Calcd:	69.98	3.67	9.07	463
			Found:	69.42	3.50	9.01	
3FP(β)NT	97	179-181	Calcd:	69.98	3.67	9.07	463
			Found:	69.49	3.37	8.95	
4FP(α)NT	98	108-110	Calcd:	69.98	3.67	9.07	463
			Found:	69.45	3.57	8.75	
3FP(α)NT	97	171-173	Calcd:	69.98	3.67	9.07	463
			Found:	69.57	3.60	9.08	

FT-IR spectrum of dialdehyde showed a characteristic band at 1703 cm^{-1} due to C=O Stretching vibration of aldehyde group. Strong absorption bands at 1593 cm^{-1} and 1229 cm^{-1} were observed due to C=N and C-O-C linkages, respectively.

^{1}H-NMR spectrum of dialdehyde 3CP(β)NT showed singlet at 9.9 δ due to two formyl protons and multiplet in the range 7.22-7.95 δ due to aromatic protons. ^{1}H-NMR spectrum of 4FP(β)NT showed singlet at 9.9 δ due to two formyl protons and multiplet in the range 7.24-7.84 δ due aromatic protons.

Mass spectrum of dialdehyde 3CP(β)NT showedmolecular ion (M+) peak at 463 which is the molecular weight of dialdehyde 3CP(β)NT.The other dialdehydes also showed molecular ion(M+) peak at 463.

The elemental analysis data of dialdehydes was in good agreement with the calculated values.

Synthesis of s-triazine containing polyazomethines.

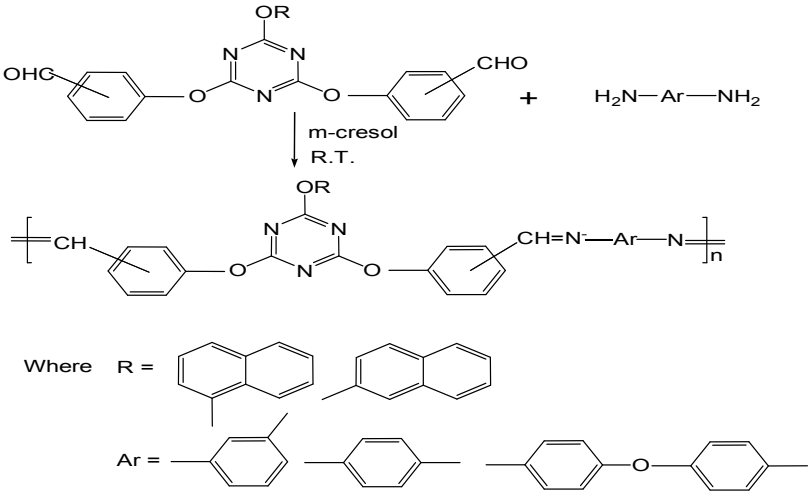
As an example synthesis of polyazomethine PAZ-1 is described below.

Into a three necked 100 ml round bottom flask fitted with a nitrogen inlet, a dropping funnel, a magnetic stirring bar and a guard tube was added 4FP(β) NT (2.315 g, 5 mmol) and 10 ml freshly distilled m-cresol under stream of nitrogen. The clear solution obtained was cooled to 20^{0}C and PPD (0.540 g, 5 mmol) was added at once. The polymerization was continued at this temperature for 24 hours. After this period the reaction mixture was poured into methanol (500 ml). The precipitated yellow powder was filtered and washed with methanol (3×100 ml). Finally the polymer was dried in vacuum at 100^{0}C for 6 hours.

RESULTS AND DISCUSSION

Synthesis of s-triazine containing polyazomethines

Ten new s-triazine containing polyazomethines were synthesized by polycondensation of equimolar quantities of dialdehydes, namely, 4FP(β)NT, 3FP(β)NT, 4FP(α) NT and 3FP(α) NT with diamines, namely, PPD and MPD in m-cresol (**Scheme-2**) The resulting polyazomethines were obtained in excellent yields. (**Table-2**) The polymerization proceeded homogeneously in m-cresol; however, the low molecular weight polymers were obtained.



Scheme-2 Synthesis of s-triazinecontaining polyazomethines

Table-2: -Synthesis of s-triazine containing polyazomethines

Polymer code	Dialdehyde	Diamine	Yield, %	$\eta_{(inh)}$ [a] (dl/g)
PAZ-1	3FP(β)NT	PPD	95	0.10
PAZ-2	3FP(β)NT	MPD	99	0.14
PAZ-3	4FP(β)NT	PPD	99	0.12
PAZ-4	4FP(β)NT	MPD	94	0.19

a = η_{inh}measured at a concentration 0.5 dl/g in m-cresol at 30±0.1^{0}c

Structural Characterization of Polyazomethines

FT-IR spectroscopic analysis

Figure-1 shows FT-IR sprectrum of polyazomethine PAZ-4. It depicted a characteristic C=N stretching absorption band at 1614 cm.$^{-1}$ The absorption band at 1544 cm^{-1} and 1210 cm^{-1} were observed due to C=N of the s-triazine ring and C-O-C linkages, respectively.

X-ray Analysis

X-Ray diffraction studies **(Figure-2)** indicated that all polyazomethines prepared in the present study were amorphous in nature.

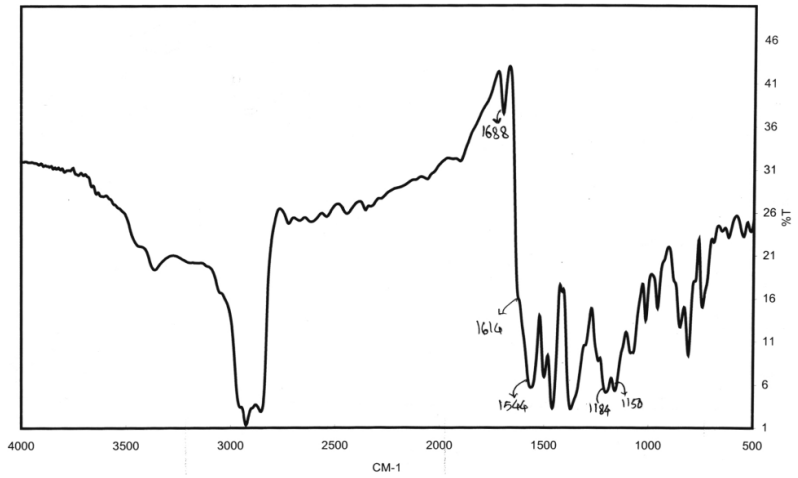


Figure-1 FT-IR sprectrum of s-triazine containing polyazomethine PAZ-4

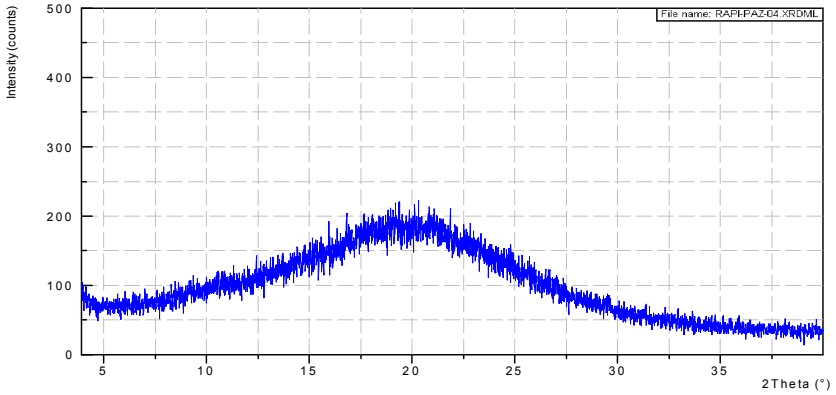


Figure-2 X-Ray diffractograms of s-triazine containing Polyazomethines PAZ-4

Properties of s-triazine containing polyazomethine

Solubility of s-triazine containing polyazomethine

The solubility behaviour of polyazomethine was evaluated at 1%(w/v) concentration in organic solvents. All polyazomethine were insoluble in common organic solvents such as chloroform, DCM, as well as dipolar aprotic solvents, such as DMF, DMAc, DMSO, NMP and HMPA. However, they were soluble in m-cresol and sulphuric acid. (**Table-3**)

Thermal behaviour of s-triazine containing polyazomethines

The thermal behavior of polyazomethines was evaluated by thermogravimetric analysis in nitrogen at a heating rate of 10^0c/min. The TG curves of representative four polyazomethines are shown in **Figure-4**The results indicated that the heat resistance temperature (IDT) of polyazomethines vary in the range of 260-410^{0}C. Thus, these polyazomethines exhibited fairly good thermal resistance property.

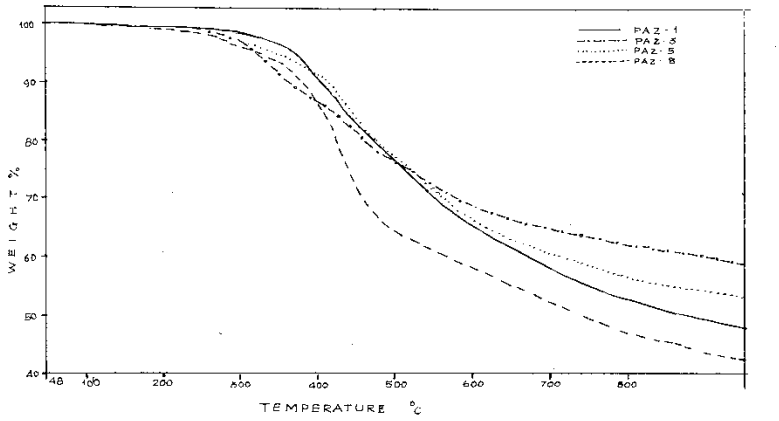


Figure-4 TG curves of s-triazine containing polyazomethines

Thermal behaviour data of s-triazine containing polyazomethine

Polyazomethine	Temperature for various % decomposition (^{0}C) IDT	10	20	30	40	50
PAZ-1	312	371	468	609	---	---
PAZ-2	260	325	400	520	650	---
PAZ-3	285	379	439	475	625	843
PAZ-4	344	361	406	444	528	717

Table-3 Solubility data of s-triazine containing polyazomethines

Polymer	Solvents						
	DMF	DMAc	DMSO	NMP	HMPA	m-cresol	H_2SO_4
PAZ-1	--	--	--	--	--	+	+
PAZ-2	--	--	--	--	--	+	+
PAZ-3	--	--	--	--	--	+	+
PAZ-4	--	--	--	--	--	+	+

+ = Soluble at room temperature -- = Insoluble

CONCLUSIONS

s-Triazine containing polyazomethines were synthesized from corresponding dialdehydes by polycondensation with PPD and MPD in m-cresol.Inherent viscosity values for polyazomethines synthesized varied in the range 0.10-0.19 dl/g indicating low molecular weights.

Polyazomethines were amorphous in nature and soluble in m-cresol andH_2SO_4 at room temperature.

The polyazomethines showed similar pattern of decomposition and the values of IDT ranged between 260-344^{0}C.The values for 10% weight loss ranged between 361-379^{0}C in nitrogen atmosphere.

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