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

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ABSTRACT:-

A series of s-triazine containing polyesters containing naphthoxy pendent groups were synthesized from four diacidchlorides namely 2, 4 Bis (¾ chlorocarbonylphenoxy) 6-α/β-naphthoxy s-triazines and bisphenol-A by phase transfer catalyzed interfacial polycondensation method. Polyesters were obtained in good yields and characterized by solubility test, viscosity measurements, RTIR, ^{1}NMR, X-ray diffraction, and TGA analysis. The polyesters were found to have viscosities in the range 0.30 to 0.64 dl/g in chloroform at 30^{0}C. Some of them exhibit film forming property. All polyesters were soluble in solvents chloroform, dichloromethane, trichloroethane, DMF, DMAc, NMP and pyridine. Thermogravimetric analysis of polyesters indicated no loss bellow 360^{0}C under nitrogen atmosphere.

KEYWORDS: - 2, 4 Bis(¾chlorocarbonylphenoxy) 6-α/β-naphthoxy s-triazines, s-triazine, polyesters, phase transfer, Interfacial polycondensation.

INTRODUCTION

The polyarylates have found applications in wide variety of areas by virtue of their attractive electrical and mechanical properties. Aromatic polyesters exhibit good thermal stability, solvent resistance and good mechanical properties and are therefore applied widely in the aviation, automobile and electronic industries.[1, 2] However, most polyarylates encounter processing difficulties due to their high glass high transition temperature or melting temperatures coupled with insolubility in common organic solvents.[3, 4] Several approaches have been adapted to improve the processability of aromatic polyesters.[5-21]

Replacement of the conventional monomers with ones containing bulky pendent group or Introduction of heterocyclic ring in the backbone of the polymer chain or Introduction of flexible linkages in the main chain or as pendent group.

The objective of the present work was to synthesize a series of polyester from s-triazine containing diacid chlorides with α- or β-naphthoxy as pendent groups and bisphenol-A.

SYNTHESIS OF S-TRIAZINE CONTAINING DIACID CHLORIDE

A representative synthesis of 2,4-bis (4-chlorocarbonylphenoxy) 6-β-naphthoxy s-triazine [4CCP(β) NT]:- Into a 100 ml round bottom flask fitted with a reflux condenser having a guard tube and a stirring arrangement were added 2,4-bis (4-carboxyphenoxy) 6-β-naphthoxy s-triazine [4CP(β) NT] (4.95

g, 0.005 mol) and 50 ml thionyl chloride. The mixture was heated at reflex for two hours and then one drop of dry DMF was added. Heating was continued further for two hours. The excess of thionyl chloride was removed under reduced pressure at 40-50^{0}C.The crude product obtained was recrystallized by dissolving in dry $CHCl_3$ and pouring into dry hexane

The same procedure was followed for the synthesis of other diacid chlorides namely 2,4-bis (3-chlorocarbonylphenoxy) 6-β-naphthoxy s-triazine [3CCP(β)NT], 2,4-bis (4-chlorocarbonylphenoxy) 6-α-naphthoxy s-triazine [4CCP(α)NT] and 2,4-bis (3-chlorocarbonylphenoxy) 6-α-naphthoxy s-triazine [3CCP(β)NT].

Synthesis of s-triazine containing polyesters

A representative procedure for synthesis of polyester is described below. Into a 100 ml two necked round bottom flask equipped with a high-speed mechanical stirrer, and an additional funnel, BPA (1.14 g, 5 mmol.) dissolved in 1N NaOH (20 ml) was charged. Thereafter, BTEAC (60 mg) was added to reaction mixture. A solution of 4CCP(β)NT (2.66 g, 5 mmol) dissolved in dry dichloromethane (25 ml) was added in one lot to the reaction mixture which was cooled to 10^{0}C and the mixture was stirred vigorously at 10-15^{0}C for one hour. The reaction mixture was poured into methanol (500 ml), the precipitated polymer was filtered and washed several times with water and methanol. The polymer was dissolved in chloroform and reprecipitated in methanol, filtered and dried at 80^{0}C under reduced pressured for 6 hours.A similar procedure was followed for synthesis of other polyesters.

RESULTS AND DISCUSSION

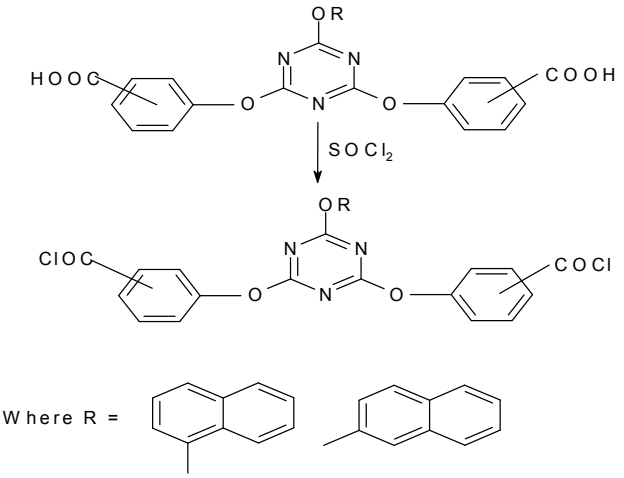
Synthesis of s-triazine containing diacid chlorides.

The diacid chlorides were synthesized from the corresponding diacids by refluxing them with excess of thionyl chloride (**Scheme-1)**. All the diacid chlorides were obtained in nearly quantitative yields and purified by dissolving in dry $CHCl_3$ and pouring in to dry hexane

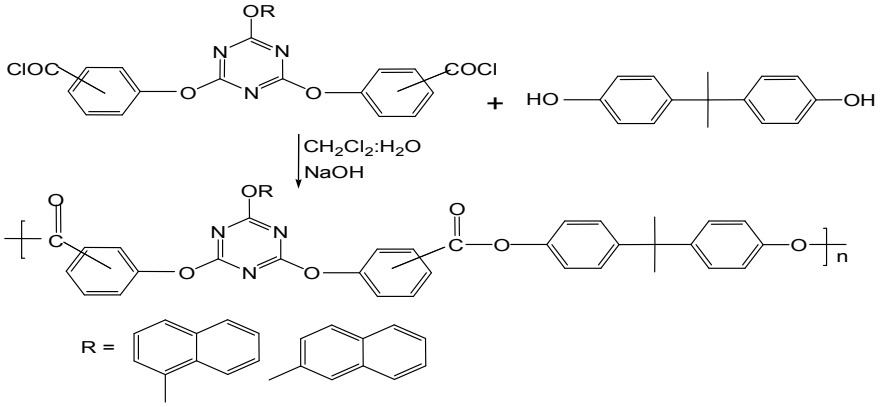
The physical characteristics and elemental analysis data of diacid chlorides are given in **Table-1**

Synthesis of s-triazine containing polyesters.

Scheme-2 illustrates the synthesis of polyesters from s-triazine ring containing diacid chlorides and bisphenol-A.Phase transfer catalyzed two phase polycondensation of diacid chlorides, namely, 4CCP(β)NT, 3CCP(β)NT, 4CCP(α)NT and 3CCP(α)NT with bisphenol-A in the presence of BTEAC as a phase transfer catalyst was used to synthesize polyesters. The physical properties of polyesters are given in**Table-2**. Polyarylates were obtained in almost quantitative yields and some of them exhibited film-forming properties. The films cast from chloroform solution were tough, transparent and flexible in nature. Polyarylates exhibited viscosities in the range 0.30-0.64 dl/g.



Scheme-1



Scheme-2 Synthesis of s-triazine containing polyesters.

Table-1 Physical characteristics ofs-triazine containingdiacid chlorides

Diacid chloride	Yield (%)	M.P (^{o}c)	Elemental Analysis	C	H	N	Cl	M^{+}
4CCP(β)NT	99	185-187	Calcd:	60.91	2.84	8.49	13.39	532
			Found:	60.80	3.00	7.87	12.97	
3CCP(β)NT	97	171-173	Calcd:	60.91	2.84	8.49	13.39	532
			Found:	61.30	3.05	7.90	12.90	
4CCP(α)NT	98	100-102	Calcd:	60.91	2.84	8.49	13.39	532
			Found:	60.80	2.75	8.15	13.32	
3CCP(α)NT	97	153-155	Calcd:	60.91	2.84	8.49	13.39	532
			Found:	60.75	3.00	7.90	12.97	

Table-2 Synthesis of s-triazine containing polyesters.

Polyester	Diacid chloride	Diphenol	Yield,%	Viscosity η^{a}_{inh} dl/g
PES-1	4CCP(β)NT	BPA	98	0.64
PES-2	3CCP(β)NT	BPA	97	0.44
PES-3	4CCP(α)NT	BPA	98	0.32
PES-4	3CCP(α)NT	BPA	96	0.30

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

STRUCTURAL CHARACTERIZATION

Spectroscopic analysis

The formation of polyester was confirmed by FT-IR and ^{1}H-NMR spectroscopy. The ester carbonyl band was observed at 1738 cm^{-1}. Strong absorption band at 1567 cm^{-1} and 1203 cm^{-1} due to s-triazine nucleus and C-O-C linkages, respectively were observed. The other absorptions at 1462 cm^{-1}, 1413 cm^{-1} and 811 cm^{-1} characteristics of s-triazine ring were also observed**(Figure-1)**

^{1}H-NMR spectrum of polyester showsA singlet at 1.71δ represents methyl protons and multiplet in the range 7.13-8.2δ represents aromatic protons**(Figure-2)**.X-Ray diffraction pattern of polyesters (**Figure-3**) indicated that all polyesters were amorphous in nature.

Figure-1

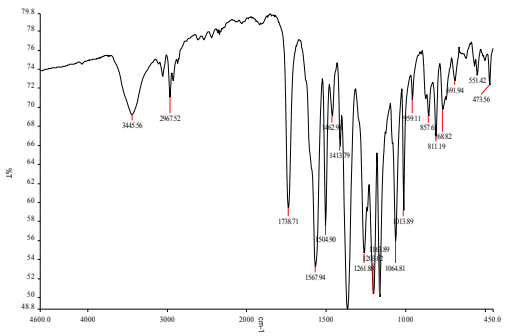


Figure-2

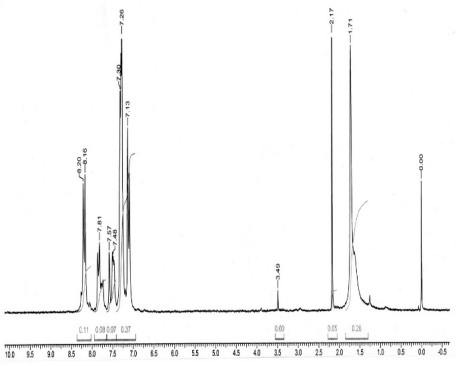
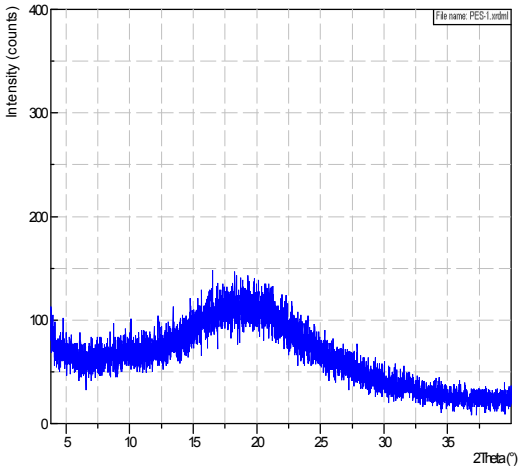


Figure-3



Properties of s-triazine containing polyesters.

Solubility of s-triazine containing polyesters.

Solubility of polyesters was tested in various organic solvents at 3 wt% (w/v) concentration and the data is summarized in **Table-3**.All polyesters were soluble in dichloromethane, chloroform, tetrachloroethane, DMF, DMAc, NMP and pyridine.

Thermal behavior of s-triazine containing polyesters.

Thermogravimetric analysis of polyesters was performed on Perkin-Elmer TGA-7 at a heating rate of 10^0C/minute under nitrogen atmosphere **Table-4** summarizes the thermal behavior data of polyesters.Polyesters showed single step decomposition behaviour. (**Figure-4**) It was observed that the initial decomposition temperature varied in the range 360-419^{0}C indicating reasonable thermal stability for these polymers.

Table-3 Solubility data of s-triazine containing polyesters.

Polyesters	**Solvents**							
	DCM	**TCE**	**$CHCl_3$**	**DMF**	**DMAc**	**NMP**	**Pyridine**	**MeOH**
PES-1	++	++	++	++	++	++	++	-
PES-2	++	++	++	++	++	++	++	-
PES-3	++	++	++	++	++	++	++	-
PES-4	++	++	++	++	++	++	++	-

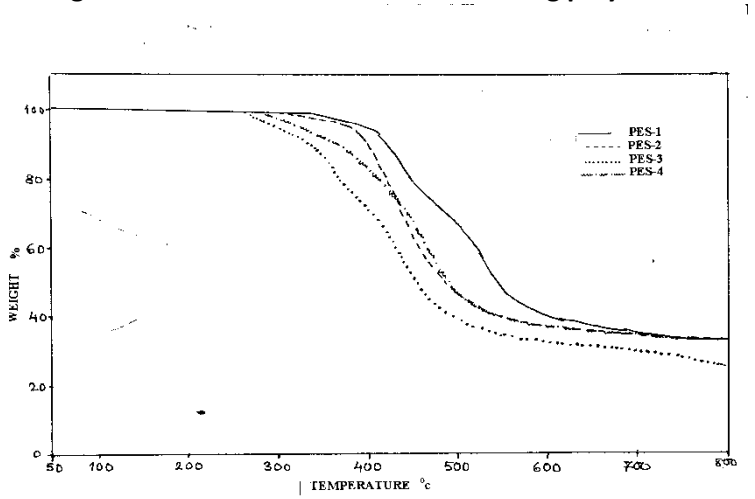
++ = Soluble at room temperature - = Insoluble

Table-4 Thermal behaviour data of s-triazine containing polyesters.

Polyester	Temperature for various % decomposition in ^{0}C					
	IDT	10	20	30	40	50
PES-1	413	423	456	500	524	547
PES-2	419	428	453	478	494	531
PES-3	360	356	394	534	549	584
PES-4	391	394	444	475	500	525

IDT =Initial Decomposition Temperatur

Figure-4 TG curves of s-triazine containing polyesters.



CONCLUSIONS

s-Triazine containing polyesters were synthesized from corresponding diacidchlorides by condensing them with BPA, using interfacial polycondensationmethod in the presence of a phase transfer catalyst. Inherent viscosity values for polyesters were in the range 0.30-0.64dl/g indicating formation moderate molecular weights. Polyesters were amorphous in nature and dissolved readily in a variety of organic solvents at room temperature. Polyesters showed similar pattern of decomposition and the values of IDT ranged between 360-419^{0}C.The values for 10% weight loss ranged between356-428^{0}C in nitrogen atmosphere.

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