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Synthesis of aromatic poly (ester-amide)s via soluble precursors derived from various diamines

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ABSTRACT

A synthesis of aromatic polyester amides has been done with interfacial-polycondensation using aliphatic as well as aromatic diacid-chlorides of terephthaloyl chloride and isophthaloyl chloride through amide containing diol in a chloroform/water system. Based on FTIR, ^{1}H NMR, ^{13}CNMR and XRD these polymers have been characterized spectroscopically. Synthesized poly (ester-amide)s was studied by physical methods such as solubility, inherent viscosity and thermodynamically by TGA-DSC analysis. To conclude the present paper polyester-amides demonstrate good thermal stability.

1. Introduction

The prime importance of high performance polymer having good mechanical and heat resistance properties show less processability.[1] High glass transition temperature of polyester-amide due to their structural combination of ester and amide therefore they shows combined properties of both of them.[2-4] Amide group having double bond character with extensive hydrogen bonding cause the rigidity in the polymer chain.[5-8] Aromatic as well as aliphatic poly(ester-amide)s shows basic properties which influences lot of work done on it over the past few decades.[9-12]. For the engineering plastic poly(ester-amide)s which one is the high performance polymer called high modulus fibre.[13-15].Therefore this important aspect keeping in mind we have synthesised this poly(amide-ester)s by interfacial polycondensation method using diacid chloride amide containing diol. This study accounts synthesised commotion of polyester amides using inter-facial poly-condensation primarily with aliphatic and aromatic diacid chlorides (terephthaloyl chloride, isophthaloyl chloride,) along with various diol having different moiety i.e. introduction of heterocyclic group, ether, sulphone linkages which increases processability without affecting thermal stability.

2. Materials and methods

2.1 Materials

Terephthalic acid (TPA) and isophthalic acid (IPA) were used after purification. Likewise, the following essential chemicals such as (benzyl chloride, (ODA), hydrochloric acid, 4, 4-'diamino diphenyl sulphone (SDA), sulphuric acid, p-phenylenediamine, sodium bicarbonate, m-aminoacetophenone, sulphur from(S.D.Fine.), sodium hydroxide, Thionyl chloride, acetone, pyridine, ethanol, methanol, chloroform) have also been employed subsequent to suitable distillation and decontamination, if essential. Bisphenol-A (BPA) was repeatedly crystallized from 50% aqueous acetic acid. Later on, after meticulously washing with water and drying the crystals have been filtered carefully. It has been applied following re-crystallizing from benzene.

2.2 Characterization

By employing thermo scientific nicolet iS 10 Smart IR the IR spectra was documented with 4 cm^{-1} resolution together with 32 scans. ^{1}HNMR spectra were recorded with 400 and 100 MHz from Bruker for ^{13}C measurements using $CDCl_3$ or DMSO solvent. Finally, with a10ºC/min heat velocity in a nitrogen atmosphere from 60 to 1000ºC the Thermo gravimetric-analysis (TGA) had also been conducted with Perkin-Elmer TGA-7 system.

3. Monomer synthesis

3.1 Aromatic acid chloride monomers

The synthesization procedure of Isophthaloyl chloride (IPC) and Terephthaloyl chloride (TPC) has been done. It has been synthesized by a novel method wherein a little amount of pyridine was applied to channel the consternation effect of its equivalent acids like dicarboxylic along with thionyl chloride as excess acid. In the end, crystallizing through n-hexane they have been purified.

3.2 Aromatic diol monomers

Synthesis of various diol i.e. (HPPTBA, BAPTHBA, HPPBA, BSPHBA) by Yamazaki polycondensation method as per the standard procedure.(scheme 1).

3.3 Setting of synthesis polyester

This study uses aromatic diol to investigate the interfacial-polycondensation with diacid chloride. It is imperative to note that the solvent system and surfactant agents were predominantly influenced the entire reaction process of polymerisation.

Solvent structure

The process of polymerization is very crucial in which organic solvent plays an important role because it hampers on different aspects of polymerization. Some of the vital factors include: possible division in reactants and its stages, diffusion and rate of reaction for reactants; its solubility, swellings and the absorptiveness for the increasing polymer. Thus, towards polymerization a structure/method based on chloroformed/water edge was utilized. As far as the stage of polar aqueous is concerned it comprises with adequate NaOH

towards dissolving BPA totally since an active-phenolate-ion which is departing as minimum as feasible un-dissociated BPA, that might be extorted through organic-phase. Whereas, non polar phase of chloroform/dichloromethane has outstanding solvents towards diacid chloride as well as oligomer used in reactions. However, possibly two side-reactions unlike towards polymer of high-molecular weight can be confined such as i) the formulation of dichlorocarbene through an act of aqueous NaOH/chloroform and ii)the alkaline-hydrolysis of OH respectively. It is to note that the mere soluble rate in water for diacid chloride serves-up to avert it by hydrolysis from alkali adequately. Furthermore, the magnitude of the side-reaction is found considerably least in comparison to polycondensation which indemnify that both either polymerisation or hydrolysis have been seen any adverse affect.

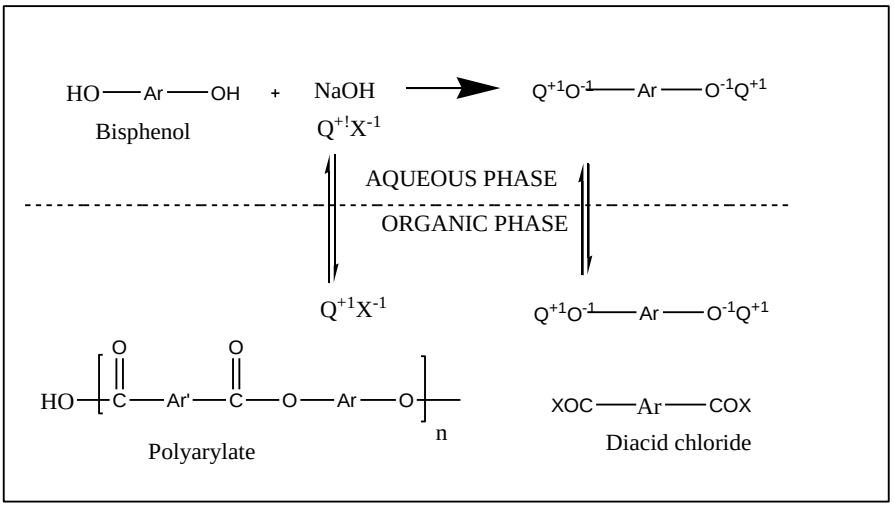
Synthesis of polyester

Considering the experience of previous investigators**,** the reactants diacid chloride (ADCl) and amide containing diol were taken in equimolar ratio, using dichloromethane-water interphase system .The stirring was vigorous and continuous and the duration of reaction was 5 min. at 30^{o}C. The results have been recorded in Table 1.

Table 1: Reaction conditions for synthesis of polyester from ADCl and BPA

Interface System: Dichloromethane/Water
Phase volume ratio : 35 mL/ 85 mL
Reactants : IPC= 0.001 mmol
BPA = 0.001 mmol
Acid acceptor : 0.025 mol NaOH
Temperature : 30ºC
Time: 5 min.
Stirring : Vigorous and continuous

In the similar manner other polyesters (PAES-1, PAES-2, PAES-3, PAES-4, PAES-5, and PAES-6) were prepared adopting the same procedure.



Scheme 1: Interfacial polycondensation

4. Results and Discussion

As a result, during last decade aromatic aliphatic polyester amides (AAPA) including fundamental and application oriented have shown potential and expanding in a relatively generous way. Irrespective of high-thermal-stability (HTS), several PEA's too show liquid-crystalline properties (LCP's). Similarly, since having high-modulus fiber (HMF's) and engineering polymer (EP's) the PEA's contains impending applicability's in the various spheres of society. Thus, in the light of above significant features the study has been undertaken with two fold objectives i) synthesizing novel PEA's based on polycondensation of aminophenol along with diacide-chloride(DC) applying interfacial-method (IM) and to ii) assess their properties comprehensively. Interfacial polycondensation of aromatic- diacid-chlorides (terephthaloyl chloride, isophthaloyl chloride,) with diols (HNPPBA, BSPHBA, HPPTBA, BAPTHBA, Bisphenol–A) and their characterization through solubility studies, intrinsic viscosity, FTIR, ^{1}H NMR, ^{13}CNMR and TGA-DSC analysis. It reveals that polyesters PAES-1, PAES-2, PAES-3, PAES-4, PAES-6 are soluble in DMAc, DMF, NMP, DMSO at room temperature while PAES-5 is insoluble in all solvents and partially soluble in nitrobenzene, m-cresol and Pyridine Further, all the polyesters containing isophthaloyl moiety are totally insoluble in dichloromethane, Toluene and ethanol.

Yield and appearance

The yield and appearance is recorded see Table.3. Yields belonging to various sample polymers including isophthaloyl moiety have ranges in between 90 to 95 %. All the polyesters are solid powders with different colors depending upon the types of aromatic diol involved. The polyesters PAES-1, PAES-2, PAES-3, PAES-4, PAES-5, and PAES-6 are white powders while other polyesters are either light to dark brown or pale yellow powders

Characterization of poly (ester-amide)s

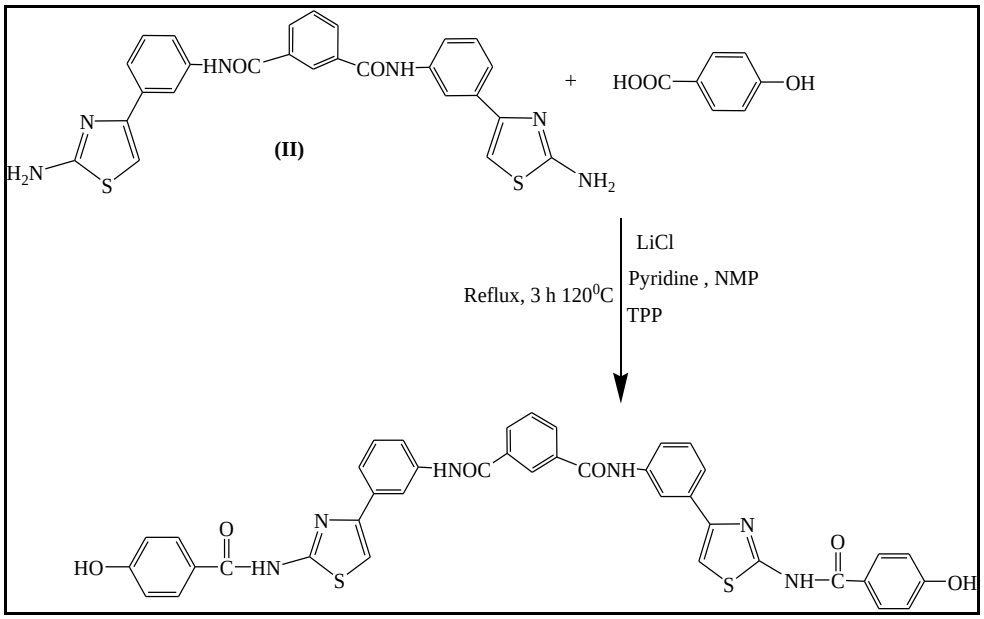
IR spectra of PAES-4

The formation of polyester from isophthalyol chloride and BAPTHBA is confirmed from the typical characteristic band at 1741 cm^{-1}(>C=O stretch band in ester) and 1644cm^{-1}(-C=O stretch of CONH linkage), 1285cm^{-1} and 1043 cm^{-1} and (C-O-C symmetric and asymmetric stretching. (Figure 1). From thermogravimetric analysis all polymers were thermally stable.

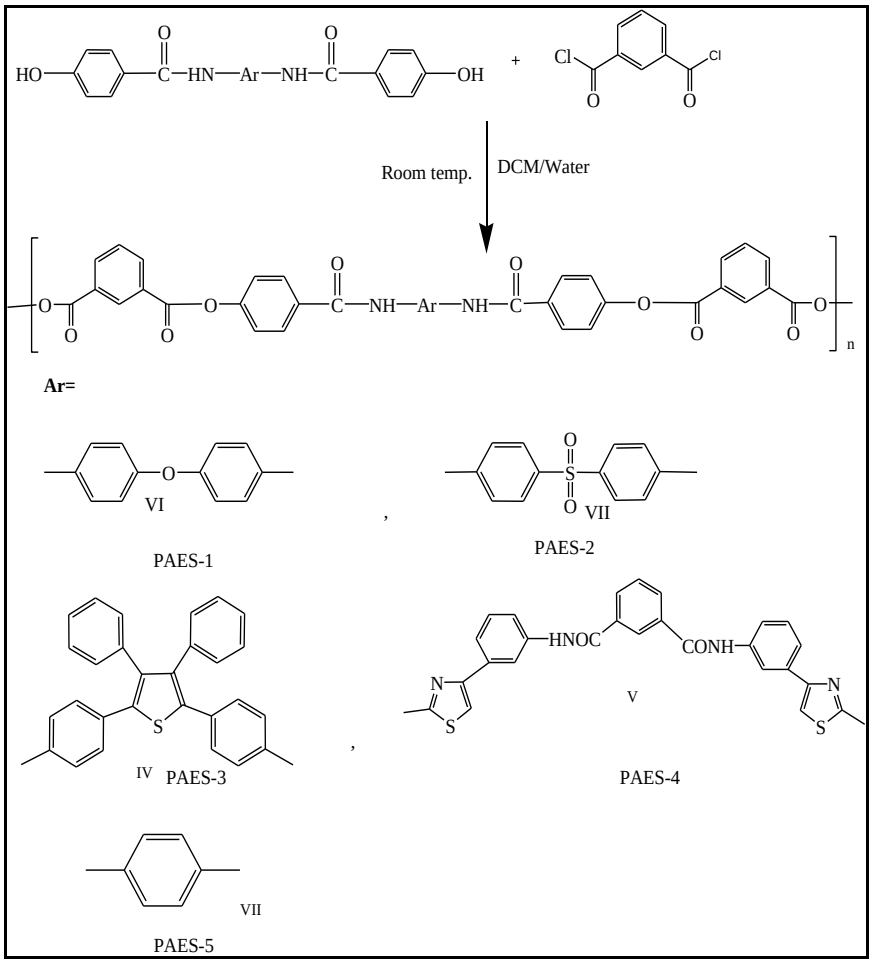
The range of temperature for the glass-transition recorded in between 167-232ºC indicates highly processable. All polymers shows % of char yield about 20-52 % shows high thermal stability.

XRD of poly (amide-ester)s

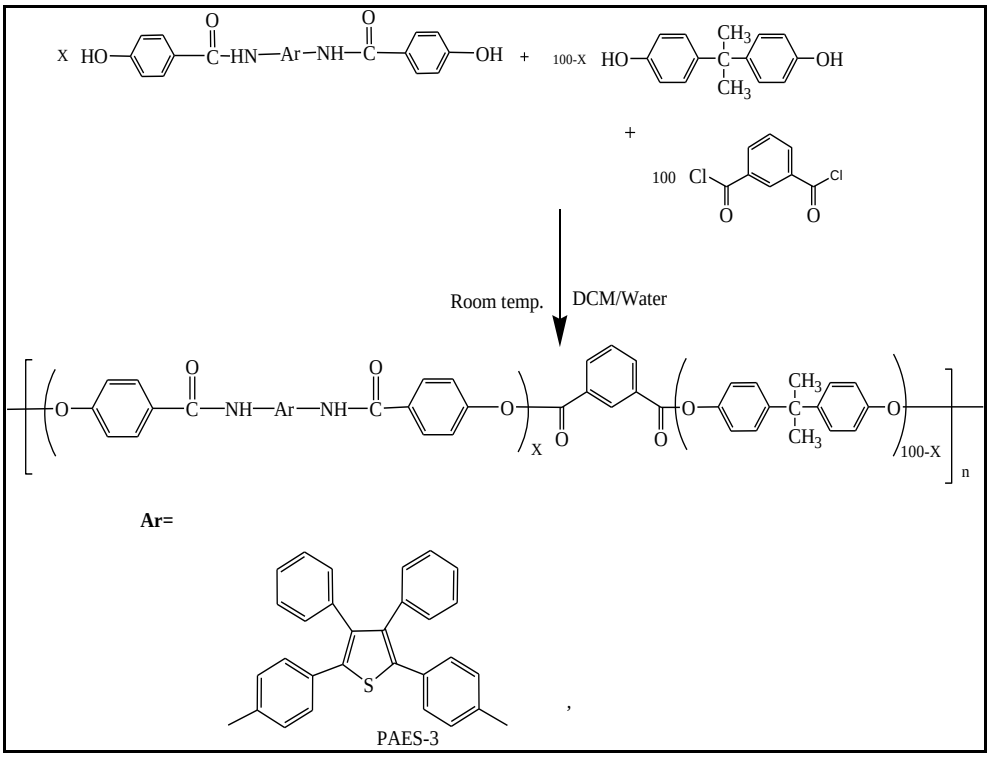
From XRD it was confirmed that the all polyesters are semicrystalline to amorphous in nature.



Scheme 1: N,N',-bis [4-3-benzoylamino-phenyl])-thiazol-2-yl)]4-hydroxybezamide (BAPTHBA)



Scheme 2: Synthesis of poly(amide-ester)s (PAES)



Scheme 3: Synthesis of copoly (amide-ester)s (PAES)from aromatic diol and isophthalyol chloride

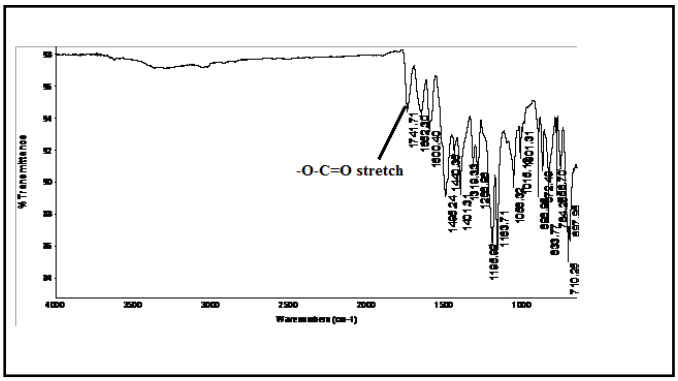


Figure 1: IR spectra PAES -4

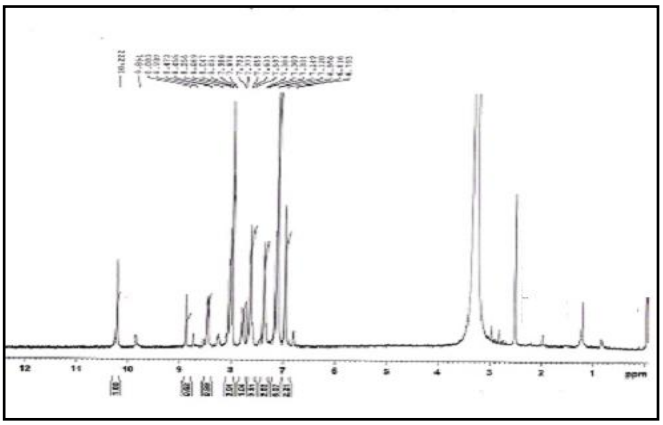


Figure 2: ^{1}HNMR spectra of PAES -4

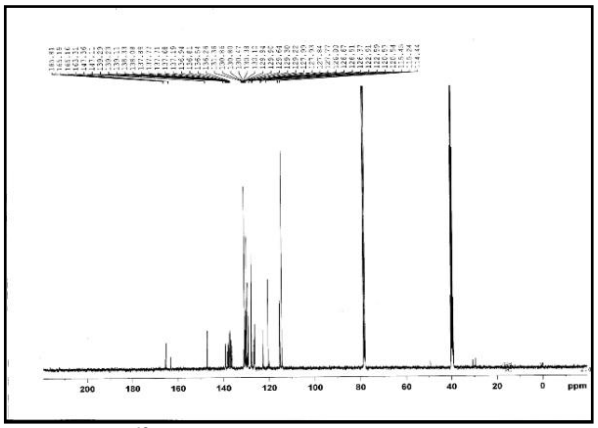


Figure 3: ^{13}CNMR spectra of PAES 4

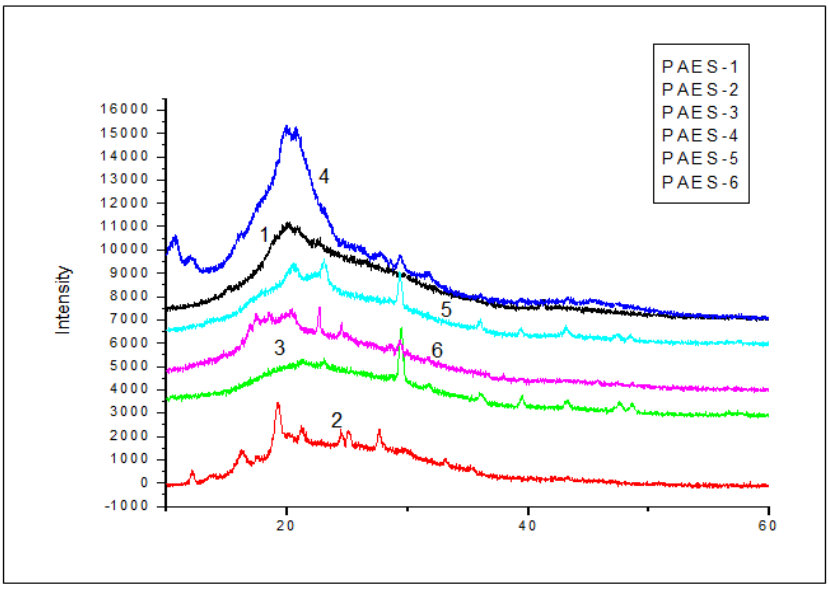


Figure 4: XRD of poly(amide-ester)s

Table 2: Yield and viscosities of poly(amide-ester)s

Polymer Code	Diol	Diacid chloride	Yield (%)	η_{inh} (dL/g)[a]
PAES-1	HPPBA	IPC	90	0.36
PAES-2	BAPTHBA	IPC	95	0.30
PAES-3	HPPTBA	IPC	95	0.60
PAES-4	BAPTHBA	IPC	95	0.54
PAES-5	HPPTBA+ BPA (75:25)	IPC	95	0.48
PAES-6	HPPTBA+ BPA (50:50)	IPC	95	0.52
PAES-7	BPA	IPC	95	0.5

Table 3: Synthesis and properties of polyesters from aromatic diol and isophthyolyl chloride

Polymer Code	Diol	Diacid chloride	T_i(°c)[b]	T_{10}(°c)[c]	T_{50}(°c)[d]	Residue at 900ºC	T_g(°c)[e]
PAES-1	HPPBA	IPC	340	410	620	38	180
PAES-2	BSPHBA	IPC	-	-	-	-	N.E.
PAES-3	HPPTBA	IPC	332	420	590	52	198
PAES-4	BAPTHBA	IPC	352	420	600	44	167
PAES-5	HPPTBA+ BPA (75:25)	IPC	410	490	610	34	190
PAES-6	HPPTBA+ BPA (50:50)	IPC	390	445	560	32	251
PAES-7	BPA	IPC	320	400	610	20.79	232

5. Conclusion

The synthesised polyesters are series of various amide linkages containing diol with IPC by interfacial polycondensation system. The poly (amide-ester)s show solubility towards polar-aprotic-solvent(PAS) like DMAc, DMSO, NMP etc. They showed good thermal stability when introduced a heterocyclic moiety like tetraphenyl thiophene, thiazole unit. The polymer PAES-4 showed Tg value 170ºC indicates processable as well as thermally stable polymer. The copolymer PAES-5 showed high Ti value low Tg value due to high percentage of PAES-3 which contain heterocyclic moiety disturbs the planarity and increases the processability.

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