



## ALIPHATIC-AROMATIC POLYESTERS DERIVED FROM ISOPHTHALOYL CHLORIDE, ETHYLENE GLYCOL AND HEXYLENE GLYCOL

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### ABSTRACT

*In the family of thermoplastic polyesters, polyethylene terephthalate (PET) is well known but polyethylene isophthalate (PEI) not explored much. In present work, we were synthesized the aliphatic-aromatic polyesters from monomeric compositions of IPC, EG and HG using phase-transfer catalyzed interfacial polycondensation technique. The synthesized polyesters were well-characterized through FTIR, <sup>1</sup>H-NMR, TGA, DSC and GPC techniques. The introduction of HG favours the solubility and loosens the stiffness of polyester because of the presence of branched methyl group. No significant difference exists among the thermal stabilities of these polyesters. Such polyesters with aforementioned properties are suitable for applications where rigidity of PET not require.*

**Keywords:** Polyesters, polyethylene isophthalate, hexylene glycol, thermal properties.

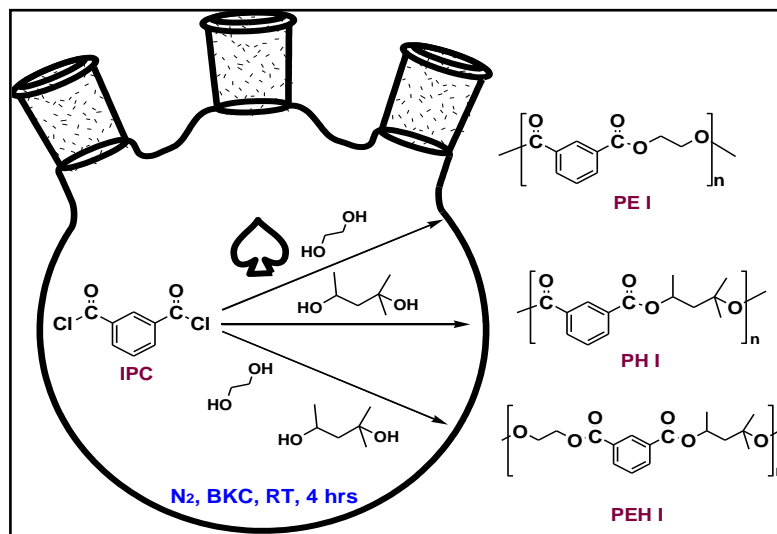
### INTRODUCTION

Poly(ethylene isophthalate) (PEI) is a relatively unexplored polyester, although its isomer, poly(ethylene terephthalate) (PET), has been researched, developed, and utilized hugely. PEI is a long, high-molecular-weight polyester chain, with a repeat unit (C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>) containing backbone phenyl rings with carboxyl groups attached in the meta 1,3 positions. PEI has not been used in industry, although the conformational characteristics of its phenyl rings would suggest potential uses in applications where PET would not suffice [1, 2]. In PET, the phenyl rings with carboxyl groups attached in the parallel 1,4 positions. Such colinear attachment of ethylene glycol diester to the phenyl rings in PET allows for flipping of the rings. Even nonlinear attachment to the naphthyl rings in Poly(ethylene 2,6 naphthalate) PEN, as compare to the PET chain appears to be less flexible. Because of the noncolinear attachment of the phenyl rings in PEI as meta position, the phenyl rings of PEI may not be flipped. Hence PEI has a lower gas permeability and possibly substituted the PET in applications where this is a factor [2]. Copolymerization resulting from the mixture of aromatic and aliphatic units is well known approach aimed at modifying the polyester structure and thermal properties. It has resulted variety of new materials with more or less success and their properties evaluated with reference to the parent homopolymer [3-5]. PEI and its copolyesters are generally difficult to process because of their high melting temperature due to rigid structure. To the best of our knowledge, no

one synthesized and studied the PEI copolyester in which hexylene glycol used as monomer. In this work, we have synthesized the poly(ethylene isophthalate), poly(hexylene isophthalate) and copolyester, poly(ethylene-co-hexylene isophthalate), with the objective of less rigid structure using versatile interfacial polycondensation technique for better applications.

### SYNTHESIS OF POLYESTERS

The isophthaloyl chloride (Aldrich, USA, recrystallized with n-hexane), ethylene glycol (SD-Fine, India) and hexylene glycol (SD-Fine, India) monomers were purchased for polyester synthesis. SD-Fine chemicals of benzalkonium chloride (BKC), dichloro methane and sodium hydroxide were procured. The polyethylene isophthalate (PEI), polyhexylene isophthalate (PHI) and copolyester, poly(ethylene-co-hexylene) isophthalates (PEHI) using 50:50 diol ratio of EG and HG, were synthesized through the interfacial polycondensation technique using as phase transfer catalyst [6] (Scheme.1). In a three-necked round bottomed flask (500 mL) equipped with a nitrogen inlet tube, a dropping funnel, and a thermometer; the EG (2.13 gms, 0.0344 mol) dissolved in NaOH solution (0.1 N, 75 mL) was placed and stirred for 15 min at RT. To this mixture, BKC (2 %w/v, 5mL) was added dropwise with stirring. After 30 min, the IPC (7.0 gms, 0.0344 mol) dissolved in DCM (25 mL) was added dropwise to the reaction mixture and vigorously stirred (1500 rpm) for 3 h at RT.



**Scheme.1: Synthesis of PEI, PHI and PEHI**  
**Table.1: Monomer compositions and characteristics of synthesized polyesters**

Polyesters	EG	HG	IPC	T <sub>i</sub> <sup>a</sup>	T <sub>50</sub> <sup>b</sup>	T <sub>max</sub> <sup>c</sup>	T <sub>m</sub> <sup>d</sup>	η <sub>inh</sub> <sup>e</sup>	M <sub>w</sub> <sup>f</sup> (10 <sup>3</sup> g/mol)	M <sub>n</sub> <sup>g</sup> (10 <sup>3</sup> g/mol)	PDI <sup>h</sup>
	Mol %										
PEI	100	00	100	219	296	476	302	0.060	-	-	-
PHI	00	100	100	170	274	358	288	0.031	3.42	3.02	1.13
PEHI	75	25	100	173	278	442	280	0.042	3.08	3.02	1.01

<sup>a</sup> initial decomposition temperature, <sup>b</sup> 50% weight loss, <sup>c</sup> maximum decomposition temperature, <sup>d</sup> melting temperature, <sup>e</sup>inherent viscosity, <sup>f</sup> weight average molecular weight, <sup>g</sup> number average molecular weight, <sup>h</sup> polydispersity index

The resultant content was poured into water; the precipitated polymer, PEI, is then filtered, washed with water and dried under reduced pressure at 40°C for 24 h. The similar procedure was followed for the synthesis of other two polyesters. Spectral characterizations of synthesized polyesters were recorded using FTIR (Shimadzu, 8400) and <sup>1</sup>H NMR (Bruker, 300MHz). The number average molecular weight (M<sub>n</sub>), weight average molecular weight (M<sub>w</sub>), and polydispersity index (PDI) of polyesters were determined using GPC (Perkin-Elmer) analysis. Thermal studies have been carried out with TGA (Shimadzu, TG50) and DSC (Shimadzu, 200F3) techniques. Physico-chemical behaviour of polyesters was discussed with solubility and viscosity studies.

## RESULTS AND DISCUSSION

The white coloured crystalline powder forms of synthesized PEI, PHI and copolyester, PEHI, have shown low molecular weight compound

(M<sub>w</sub> = ~ 3 x 10<sup>3</sup> g/mol) with PDI of ~1.1 using GPC. The absorption bands inbetween 1782-1684 cm<sup>-1</sup> (C=O stretching) and 1303-1068 cm<sup>-1</sup> (-C-O-C- stretching) in the IR spectrums of PEI, PHI and PEHI (Figure.1a) were indicated the presence of ester linkages [7]. <sup>1</sup>H NMR spectrum of PEHI was carried out in DMSO (Figure.1b). The signals of aromatic protons of the isophthalate ring were located at 8.48 ppm, 8.15 ppm, 7.65 ppm while aliphatic protons of methylene have appeared at 4.81-4.70 ppm. The signal at 1.73 ppm, 1.32 ppm, 1.10 ppm, 1.20 may be attributed to methyl protons of pentane moiety in the polyester chain. The resonance signals of methylene protons are observed at 1.91 ppm [2]. Both the techniques were confirmed the formation of copolyester, PEHI.

TGA curves of polyesters (Figure.1c) were thermally stable upto 169°-220°C with multistage degradation patterns. The initial decomposition (T<sub>i</sub>) of PEI at 220°C, PHI at 170°C and PEHI around 173°C indicates that

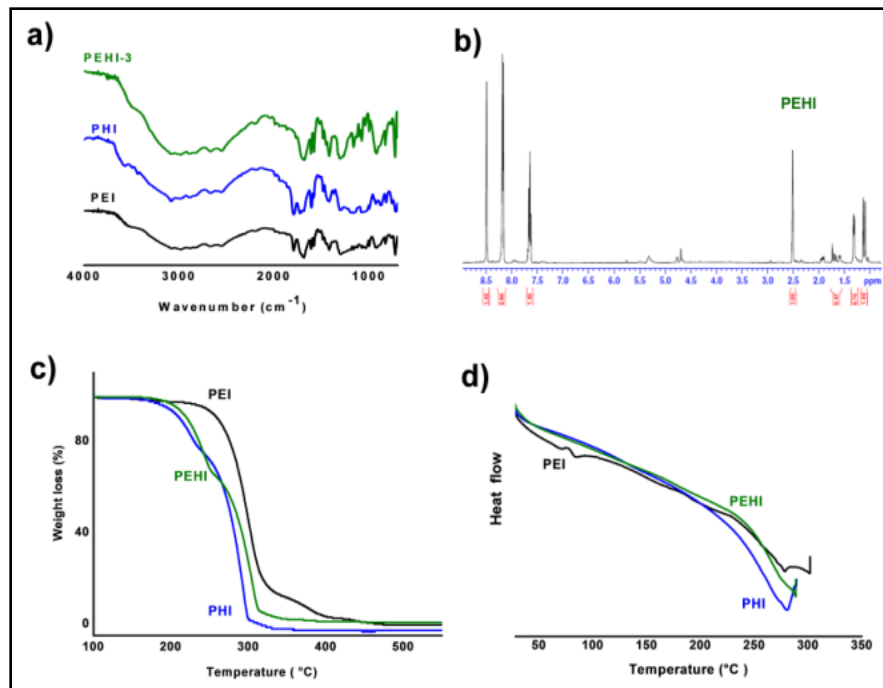


Figure.1: a) FTIR spectra, b) <sup>1</sup>H-NMR spectra of PEHI, c) TGA curves and d) DSC thermograms of synthesized PEI, PHI and PEHI

hexylene moiety decreases the resonance in the polymer chain. The maximum thermal degradation ( $T_{max}$ ) of PEI has started from 470°C and PHI from 360°C. But copolyester, PEHI, shows the  $T_{max}$  from 445°C. It was clearly indicated the stability of PEHI better than PHI [8]. From the DSC thermogram (Figure.1d), it can be concluded that melting temperature ( $T_m$ ) of polyesters, PHI and PEHI, containing methyl side chain was less than PEI (not having methyl side chain). Results have proved that the rigidity of the polyester molecule reduces in the presence of HG.

Synthesised PHI and PEHI were easily soluble in aprotic polar solvents like THF, DMSO, DMF and insoluble in chlorinated solvents like DCM, chloroform as well as in water and HCs of toluene type solvents [9, 10]. But PEI has not been solubilized in the used solvents due to its rigid aromatic nature. Solubility studies were clearly proved that the introduction of methyl side chain in the parent polyester chain increases the solubility parameters. The decrease in inherent viscosity of HG based polyesters than PEI also confirmed the less rigidity in the molecule.

## CONCLUSION

The aliphatic-aromatic polyesters, PEI, PHI and PEHI were successfully synthesized using phase-transfer catalyzed interfacial polycondensation technique and well-characterized through FTIR, <sup>1</sup>H-NMR, TGA, DSC and GPC techniques. Addition of HG with EG in the copolyester PEHI has shown better solubility and decreases the stiffness of polyester. Not much compromised in thermal stabilities of the polyesters was also fruitful for its applications. Copolyesters with flexi properties are better processable and applicable where PET not found better. Such flexible polyesters consumption has increased substantially in fibers and molding resins due to the strong demand for textile applications, as well as in food packaging and bottle markets.

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