

Synthesis of high T_g and organosoluble Poly(N-Arylenebenzimidazole ether imide) copolymers by C-N/ C-O coupling reaction

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Introduction

Polybenzimidazoles (PBIs) and polyimides (PIs) are well known heterocyclic high performance polymers for high temperature aerospace applications due to their outstanding thermal, mechanical and dielectric properties (Fig 1).^[1-2] Polyimides have gain attraction as a class of advanced materials because of their outstanding thermal stability, good insulation properties with low dielectric constant, superior chemical stability and good adhesion to common substrates. These characteristics make them useful for various applications such as semiconductor and electronic packaging industries. However, difficult handling of poly (amic acid) (PAA) precursors and limited solubility of fully imidized PIs in organic solvents, restricted their applications in specific fields. Therefore, numerous research efforts have been reported for the development of organosoluble PIs by modification of the structure.^[3]

PBIs have potential use for various industrial applications e.g. high temperature resistant fibre suits, fibre spinning and reverse osmosis membranes, owing to their excellent fire retarding capacity, insulating behaviour and thermo chemical resistance without extensive loss of properties.^[4] In spite of these attractive properties, PBIs have limited applications in many fields due to their difficult processability and organosolubility since many are only soluble in strong acids on account of their rigid backbone and strong interchain interactions. Hence, several approaches are utilized to improve the processability and organosolubility by the introduction of flexible linkages in polymer chain and copolymerization of PBI e.g. PBI blends, PBI-polyamide and PBI-polyimide.^[5]

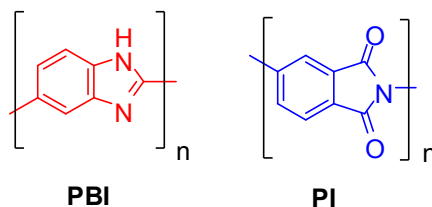
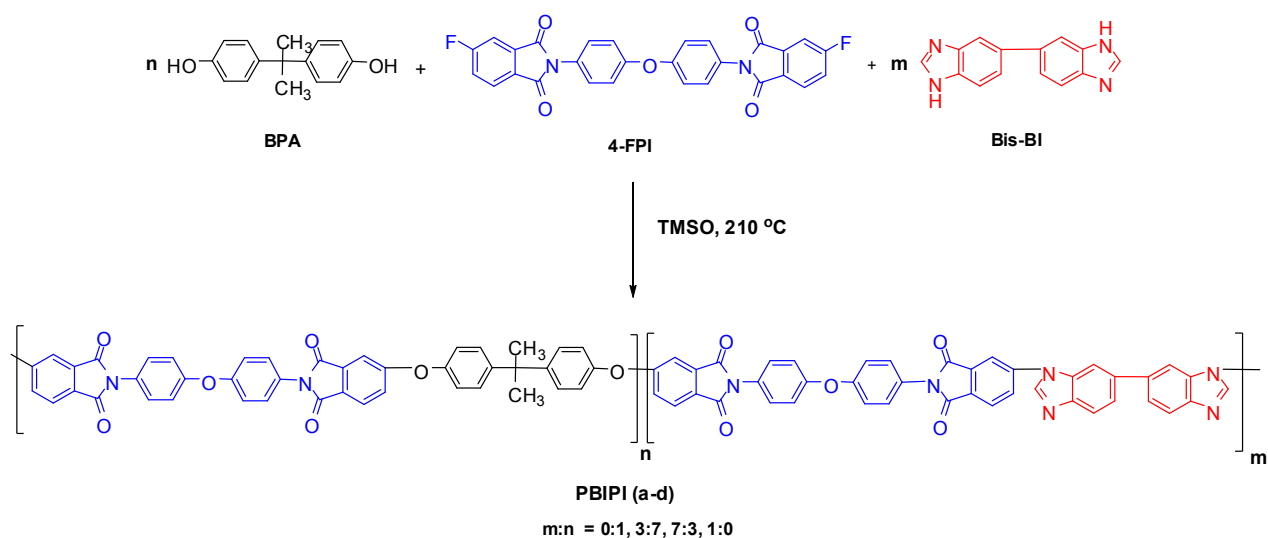


Fig 1. Chemical structures of polybenzimidazole (PBI) and polyimide (PI)

Moreover, poly(benzimidazole imides) (PBIPIs) have been reported previously by polycondensation method, exhibited high thermal and mechanical stability but limited solubility in organic solvents and poor film forming ability.^[6-8] Hergenrother and coworkers had described the synthesis of poly(arylene ether benzimidazole)s, which exhibited good organosolubility on account of ether linkage but at the expense of poor thermal stability.^[9-10] These limitations prompted us for the development of new copolymers by combining desirable features of poly(arylene ether benzimidazole)s PAEBIs and poly (benzimidazole imide)s PBIPIs.

In the present study, our focus is to synthesize poly(N-arylenebenzimidazole ether imide)copolymers **PBIPI** with high glass transition temperature (T_g) and good solubility. A series of copolymers prepared by using different feed ratio of bisphenol-A (BPA) and bis benzimidazole (Bis-BI) with 4,4'-bis(4-fluoro phthalimido)diphenyl ether(4-FPI). Bis-BI possesses both proton-donor (-N-H) and proton acceptor (=C-N-) sites. In polymerization, (-NH) site of Bis-BI has been substituted via C-N coupling reaction with activated

phthalimide 4-FPI by aromatic nucleophilic substitution polymerization (SNAr). The solubility, thermal and mechanical properties of these copolymers have been also investigated.



Scheme 1. Synthesis of poly(*N*-arylenebenzimidazole ether imide)s **PBIPI (a-d)**

Results and Discussion:

Bis-BI was prepared by condensation reaction of 3, 3'-diamino benzidine and formic acid. 4,4'-Bis(4-fluoro phthalimido) ether (4-FPI) was synthesized by condensation of 4,4'-oxydianiline(ODA) and 4-fluoro phthalic anhydride. **PBIPI (a-d)** copolymers were synthesized by aromatic nucleophilic substitution of 4-FPI with (–N–H) and (–O–H) sites of bisbenzimidazole and bisphenol A, respectively (Scheme 1).

The inherent viscosities (η_{inh}) of homopolymer and copolymers were detected within the range of 0.44–0.71 dL/g, and are listed in Table 1. With the increase of Bis-BI content, η_{inh} of copolymers were observed to decrease. All copolymers **PBIPI (a-c)** gave flexible polymer films except **PBIPI-d**, as it contained only bis benzimidazole unit.

Table 1. Inherent viscosity and film forming ability of polymers

PBIPI	Feed ratio of monomers (Bis-BI:BPA)	η_{inh}^a (dL/g)	Film^b
a	0:1	0.71	Flexible
b	3:7	0.67	Flexible
c	7:3	0.63	Flexible
d	1:0	0.44	Brittle

^aInherent viscosity measured using 0.5 g/dL in NMP at 30 °C.

^bFilms were casted using 10% solution of polymers in NMP(*N*-methyl-2-pyrrolidone).

The solubility of copolymers was investigated in common organic solvents and summarized in Table 2. All copolymers exhibited significant solubility in aprotic solvents such as NMP (*N*-methyl-2-pyrrolidone), DMAc (*N,N*-dimethylacetamide), *m*-cresol and DMSO (dimethyl sulfoxide). In comparison, copolymers with high benzimidazole composition showed poor solubility in NMP, DMAc and DMSO at room temperature, whereas these were insoluble in THF (tetrahydrofuran), chloroform, and DMF (*N,N*-dimethyl formamide). This was probably due to the presence of rigid benzimidazole structure that enhanced the

backbone stiffness of resultant polymer.

Table 2. Solubility of polymers

PBIPI	Solvents						
	<i>m</i> -Cresol	NMP	DMSO	DMA	DMF	THF	CHCl ₃
a	++	++	+	++	+	+-	+
b	++	++	+	++	+-	-	-
c	++	+	+	+-	-	-	-
d	++	+	+	++	+-	-	-

The qualitative solubility was tested with 20 mg samples in 1 mL of solvent; ++: fully soluble at room temperature; +: soluble on heating; +-: partially soluble or swelling on heating; -: insoluble; DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; DMSO: dimethyl sulfoxide; NMP: *N*-methyl-2-pyrrolidone; THF: tetrahydrofuran.

Table 3. Thermal and mechanical properties of PBIPI

PBIPI	T_g^a (°C)	$T_{d5\%}^b$ (°C)		$T_{d10\%}^b$ (°C)		Char Yield ^c (%)
		N ₂	Air	N ₂	Air	
a	219	519	437	528	478	51
b	249	492	467	511	503	47
c	306	499	470	535	510	40
d	391	427	391	483	432	60

^aObtained from second heating scan of DSC with 20 °C /min heating rate.

^bTemperatures at which 5% and 10% weight loss recorded by TGA at a heating rate of 10 °C /min in nitrogen and air.

^cResidual weight at 800 °C in nitrogen.

Thermogravimetric analysis (TGA) analysis and differential scanning calorimetry (DSC) were performed to investigate the thermal properties of polymers, and results are summarized in Table 3. The thermal stability of copolymers was evaluated by TGA at heating rate of 10°C/min in nitrogen and air atmosphere. The decomposition temperature for 10% weight loss was recorded in the range of 483–528°C in nitrogen while at 432–510°C in air atmosphere. Thermal stability of **PBIPI-c** was high which could be ascribed to more benzimidazole segments in polymer chain as well as higher Mw.

The glass transition temperature (T_g) of the copolymers were observed in the range of 219-391°C following the increasing order of **PBIPI a**<**b**<**c**<**d**, as presented in Table 3. **PBIPI-d** containing only bis-benzimidazole content showed highest T_g value because of the presence of very rigid benzimidazole and phthalamide units with strong interchain interactions. While with the increase of ether linkages from BPA, the observed T_g values decreased in resulting copolymers due to the increase of chain flexibility.

The mechanical and rheology properties of copolymers are in progress.

Conclusion

A series of benzimidazole-imide copolymers **PBIPI (a-d)** containing flexible ether linkages were synthesized via aromatic nucleophilic substitution (SNAr) and characterized. All the copolymers exhibited significant solubility in common organic solvents. The T_g values increased by increasing the benzimidazole contents in copolymers. While, solubility enhanced from moderate to high in common organic solvent by increasing bisphenol feed ratio in copolymers. The obtained results demonstrated that these novel

benzimidazole-imide copolymers **PBIPI (a–d)** with ether linkage endowed high thermal stability, good solubility and can be served as high performance materials. These properties can be tailored to need for potential applications by controlling the feed ratio of bis-benzimidazole and bisphenol-A.

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