

Two-Step Synthesis of Aromatic Polybenzimidazoles via Soluble Poly(*o*-amino amide)s

Mayu HANADA (花田舞結) Yuji SHIBASAKI (芝崎祐二) Yoshiyuki OISHI* (大石好行)

*Department of Chemistry, Graduate School of Engineering, Iwate University (岩手大学)
4-3-5 Ueda, Morioka, Iwate 020-8551, Japan*

Abstract: A new synthetic method for the preparation of poly(benzimidazole) (PBI) precursors, poly(*o*-amino amide)s, from 3,3',4,4'-tetraaminobiphenyl and triazine-based active diesters have been developed. The precursors were synthesized by the polycondensation of 3,3',4,4'-tetraaminobiphenyl and triazine-based diesters in *N*-methyl-2-pyrrolidone (NMP) in the presence of LiCl with the elimination of hydroxytriazine. The pure precursors could be obtained by washing crude precursors with methanol or water to remove LiCl and hydroxytriazine. The precursors were soluble in NMP and *N,N*-dimethylacetamide (DMAc), and gave transparent and flexible cast films. The precursor films were thermally converted to the flexible and transparent PBI films which had high thermal stability with high glass transition temperatures of around 400 °C and high thermal decomposition temperatures of around 500 °C in air and low coefficient of thermal expansion of 6-16 ppm/°C. The fluorine-containing PBI films were also prepared by the two-step method from 2,2-bis(3,4-diaminophenyl)hexafluoropropane and the triazine-based diesters. The fluorine-containing PBI films showed high transparency, high glass transition temperatures of around 300 °C, and relatively lower dielectric constants of around 2.9.

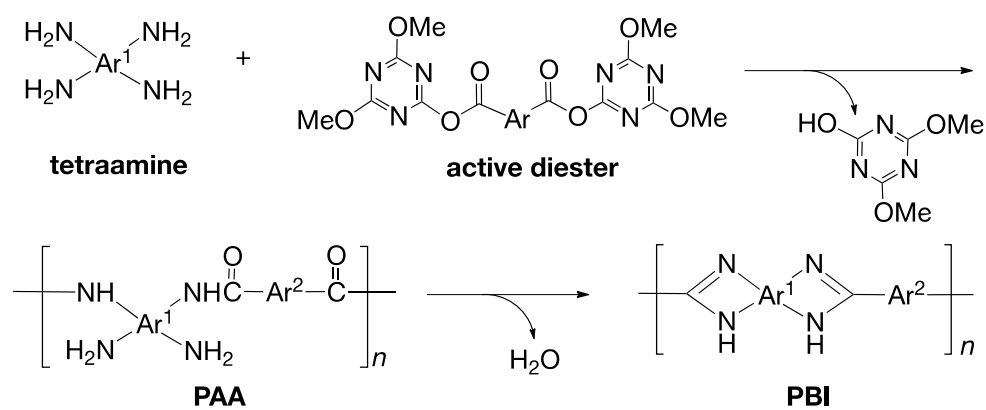
Keywords: aromatic polybenzimidazole / fluorine-containing polybenzimidazole / two-step synthesis / poly(*o*-amino amide) / soluble precursor / high thermal stability / low coefficient of thermal expansion / high transparency / low dielectric constant

1. INTRODUCTION

Polybenzimidazoles (PBI) are a class of heterocyclic polymers, which have excellent thermal, chemical, and mechanical properties. Their applications include fiber, membranes, nano-filtration, and gas separation, etc. When fabricated into membranes and doped with low vapor pressure proton conductors such as phosphoric acids, the corresponding acid-doped PBI membranes were reported as promising alternatives to traditional perfluorosulfonic acid-based membranes for the application of high-temperature proton exchange membrane fuel cells [1]. Among various PBI derivatives, meta-PBI derived from 3,3',4,4'-tetraaminobiphenyl and isophthalic acid is the most studied due to its commercial availability. However, PBI has some drawbacks such as weak mechanical properties at high acid loading and poor solubility in organic solvents. Therefore, recently, considerable research has been focused on investigating the synthesis of new PBI. One effective way to improve the performance of polymers is to introduce fluorine or fluorine-containing groups into the polymer backbone. This strategy has been widely used in the structural modifications of high-performance polymers such as polyimides, polyamides and poly(arylene ether)s. The fluorinated PBIs show good solubility in organic solvents, low water uptake, low dielectric properties, and high thermal and oxidative stability [2-5]. There are several strategies for the synthesis of PBI polymers such as melt polymerization and direct polymerization. A melt-solid polymerization method [6] is applied for the production of commercially available meta-PBI. The polymerized powder product has lower solubility. Therefore, it is resolved at high temperatures and pressures and used to produce a high-performance thermally stable fiber which is used for various fire-resistant applications. Another important synthetic approach is by direct polymerization in phosphoric acid (PPA) [7] or Eaton's reagent

(PPMA, phosphorus pentoxide/methane sulfonic acid = 1/10, w/w) [8]. The obtained PBI contains the H₃PO₄ salted structure in the polymer after polymerization. The salted PBI has to be neutralized by base treatment to make the PBI soluble in common organic solvents such as NMP or DMAc. This work-up stage was very complex and should be simplified for large volume production. Although, PBI can be successfully prepared using these methods, none of the techniques mentioned provide a two-step method to the synthesis of PBI in common organic solvents suitable for the film preparation of PBI. We reported that the triazine-based active diester was a promising monomer for the synthesis polyamides [9] and polybenzoxazoles by two-step method [10].

In this work, PBI were successfully synthesized by two-step route that involves the solution polycondensation of tetraamine with triazine-based active diester to afford soluble precursor, poly(*o*-amino amide) (PAA), followed by thermal cyclodehydration (**Scheme 1**). The present article deals with the preparation and characterization of aromatic PBI films derived from 3,3',4,4'-tetraaminobiphenyl (DAB) and fluorine-containing PBI films derived from 2,2-bis(3,4-diaminophenyl)hexafluoropropane (TA).



Scheme 1. Synthesis of PBI by two-step method.

2. SYNTHESIS AND PROPERTIES OF AROMATIC PBI DERIVED FROM 3,3',4,4'-TETRAAMINOBIIPHENYL (DAB)

Aromatic PBI from 3,3',4,4'-tetraaminobiphenyl (DAB) were prepared by two-step method (**Figure 1**). The solution polycondensation of DAB with triazine-based active diesters derived from isophthalic acid, terephthalic acid and 4,4'-biphenyldicarboxylic acid was carried out in NMP in the presence of LiCl at -10-25 °C for 24 h. The 4-amino groups were more reactive than the 3-amino groups of DAB toward the triazine-based active diesters due to the steric hindrance to yield poly(*o*-amino amide)s (PAAs) with the elimination of hydroxytriazine. The PAAs have inherent viscosities of 0.8-1.1 dL/g, number average molecular weight (M_n) of 30,000-36,000 and polydispersity index (M_w/M_n) of 2.3-2.5. The PAAs were soluble in NMP, DMAc and DMF, and afforded the transparent and flexible films cast from DMAc solutions (20 wt%). The PAA films thus obtained were subjected to thermal cyclodehydration at 410 °C for 10 min. The obtained PBI(DAB-IPT)film derived from isophthalic acid were soluble in DMAc, but other PBI films derived from terephthalic acid and 4,4'-biphenyldicarboxylic acid were insoluble in organic solvents. All the PBI films did not lose weight up to 470 °C in air and 600 °C in nitrogen, and the temperatures at which 5% weight loss was recorded were 500-525 °C in air and 630-680 °C in nitrogen. The PBIs had high glass transition temperatures between 390-410 °C and low coefficient of thermal expansion of 6-16 ppm/°C, depending on the rigidity of dicarboxylic acid component. The tensile properties of the yellow, transparent and flexible films of PBIs were measured: tensile strength of 84-114 MPa, elongation at break of 2-4%, and tensile modulus of 3.5-5.6 GPa.

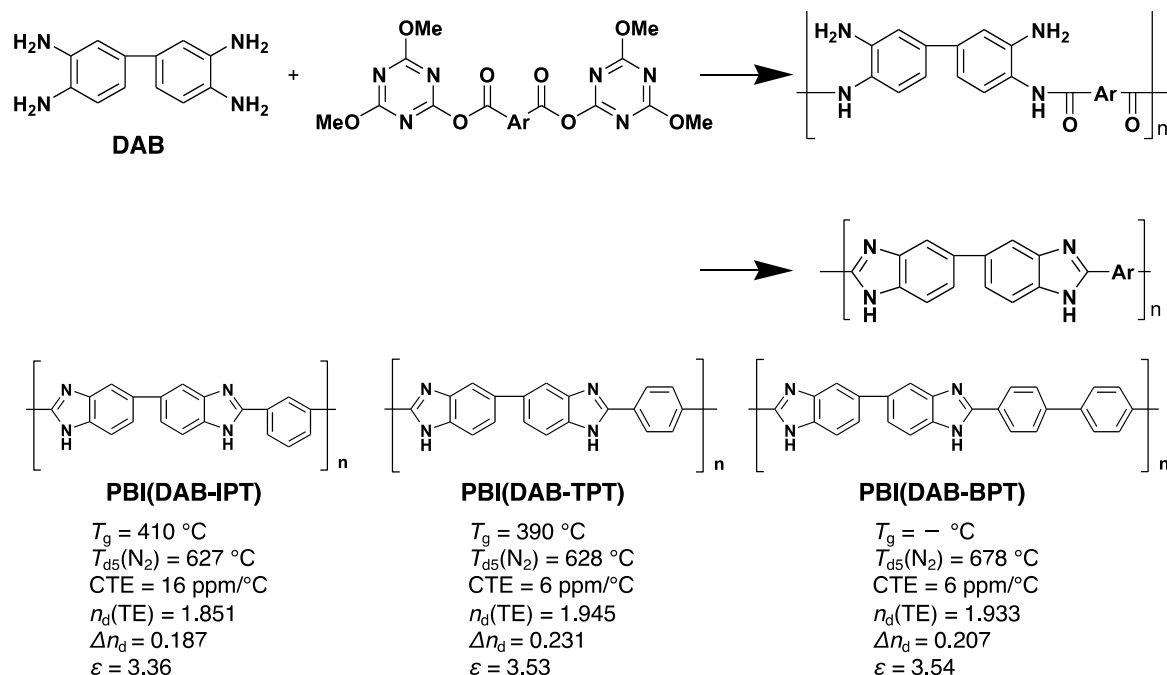


Figure 1. Synthesis and properties of aromatic PBIs.

3. Synthesis and Properties of Fluorine-Containing PBI derived from 2,2-bis(3,4-diaminophenyl)-hexafluoropropane (TA)

Fluorine-containing PBIs from 2,2-bis(3,4-diaminophenyl)hexafluoropropane (TA) were prepared by two-step method (Figure 2). The solution polycondensation of TA with triazine-based active diesters derived from 4,4'-oxydibenzoic acid, isophthalic acid and terephthalic acid has proceeded at $-10\text{--}50\text{ }^\circ\text{C}$ for 16 h to afford PAA without gelation during the polymerization. The PAAs have inherent viscosities of 0.44-0.48 dL/g, number average molecular weight (M_n) of 19,000-26,000, and polydispersity index (M_w/M_n) of 2.0-2.2. The PAAs were readily soluble in organic solvents such as NMP, DMAc, DMF, THF and acetone. The fluorinated PAAs had better solubility than the PAAs derived from DAB. The introduction of hexafluoroisopropylidene groups into the polymer backbone could improve the solubility of the PAAs. The fluorinated PBIs prepared by the thermal cyclodehydration of the PAAs were stable up to $400\text{ }^\circ\text{C}$ and the 5% decomposition temperatures of T_{d5} for the PBIs in air and nitrogen were $443\text{--}488\text{ }^\circ\text{C}$ and $491\text{--}515\text{ }^\circ\text{C}$, respectively. The thermal stability of fluorine-containing PBIs was slightly lower than that of aromatic PBIs derived from DAB. The glass transition temperatures and coefficient of thermal expansion (CTE) of the fluorinated PBIs were $373\text{--}410\text{ }^\circ\text{C}$ and $34\text{--}45\text{ ppm}/^\circ\text{C}$, respectively. PBI(TA-TPT) with rigid terephthalic acid structure showed higher T_g and lower CTE than those of PBI(TA-OBBT) and PBI(TA-IPT). The films of PBI(TA-OBBT) and PBI(TA-IPT) showed the wavelength of cutoff at around $340\text{--}350\text{ nm}$, which exhibited colorless and high transparency. On the other hand, PBI(TA-TPI) film was yellow and transparent. The refractive indices (n) of fluorinated PBI films were measured to be 1.641-1.656. The dielectric constant (ϵ) around 1 MHz of the PBI films has been estimated from the refractive index (n) according to Maxwell's equation: $\epsilon = 1.10n^2$. The refractive indices of 1.641-1.656 can be translated into the dielectric constants (ϵ) of 2.96-3.02. The dielectric constants of PBIs containing hexafluoroisopropylidene groups were lower than those ($\epsilon = 3.36\text{--}3.54$) of aromatic PBIs derived from 3,3',4,4'-tetraaminobiphenyl (DAB).

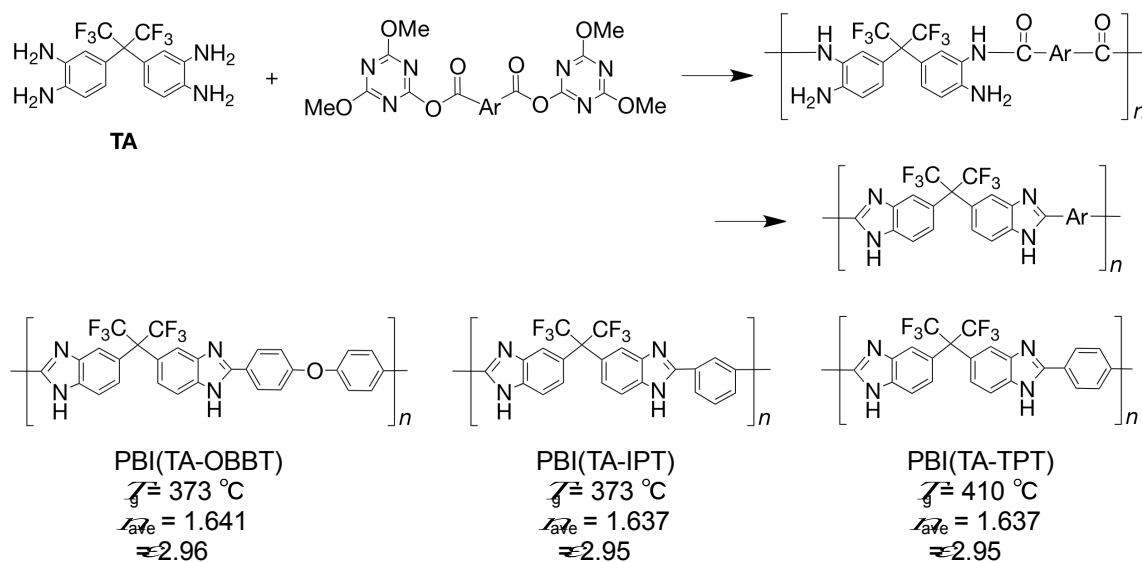


Figure 2. Synthesis and properties of fluorine-containing PBIs.

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