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## Highly gas permeable aromatic polyamides containing adamantane substituted triphenylamine

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## ABSTRACT

A series of new aromatic polyamides (PAs) containing 1-adamantanemethoxy substituted triphenylamine has been synthesized for the membrane based gas separation. The PAs were readily soluble and cast into flexible membranes (tensile strengths  $\sim 104$  MPa). All the membranes showed high thermal stability ( $440\text{ }^\circ\text{C} < T_{d10}$  in air). The permeability of  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$  through these PA membranes was investigated at  $35\text{ }^\circ\text{C}$  under an applied upstream pressure of 3.5 bar. PA 8b containing hexafluoroisopropylidene moiety exhibited high gas permeability and reasonably good permselectivity in the series ( $P_{\text{CO}_2} = 61.5$  and  $P_{\text{O}_2} = 14.2$ ,  $P_{\text{CO}_2}/P_{\text{CH}_4} = 51.25$  and  $P_{\text{O}_2}/P_{\text{N}_2} = 10.14$ ). The gas transport properties have been correlated with the polymer structures with respect to their glass transition temperature, fractional free volume (FFV) and dielectric constant values. FFV and free volume distribution were also calculated by the molecular simulation to understand the gas transport properties of the PAs.

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## 1. Introduction

Membrane-based gas separation has established as a superior, economical and efficient separation technique over other conventional methods [1,2]. Some of the important applications are separation of air for oxygen enrichment in combustion processes and medical application or nitrogen enrichment for food packaging, and the removal of carbon dioxide for natural gas “sweetening” [3]. However, high production cost of polymeric material, the limited thermal and chemical stability of the membranes under the separation process condition, along with difficulty in attaining high gas purity have limited the full development of membrane based separation [3,4]. In addition, there is an inherent trade-off between gas permeability ( $P$ ) and selectivity ( $\alpha$ ) for a pair of gases that limits the large scale applications of this technique [5]. Gas permeation through the dense polymer membranes proceeds by solution diffusion mechanism depending on the chain segmental mobility, which creates transient opening of the leap channels of effective size through which the gas molecules permeate [6]. However, there is no strict “design rules” for the polymer to obtain optimal gas separation [7]. A significant amount of research both from academia and industry was carried out to understand the relation between the polymer structure and the gas permeability [5]. Although several

classes of polymers had already been developed for gas separation purpose but only a few had found actual application in industrial gas separation plants. Thus, to develop polymeric membranes with high permeability and high gas selectivity for different gas pairs (e.g.,  $\text{CO}_2/\text{CH}_4$ ,  $\text{O}_2/\text{N}_2$ , etc.) along with superior physical and mechanical properties is a great challenge both in academia and in industry.

So far, polyimides are the most investigated candidates as the materials for gas separation applications. High gas selectivity for different gas pairs (e.g.  $\text{CO}_2/\text{CH}_4$ ,  $\text{O}_2/\text{N}_2$ , etc.) along with excellent thermal stability, film forming ability and mechanical strength made polyimides promising materials for gas separation applications [8]. Polyamides (PAs) are also well known for their excellent thermal and mechanical stability. Although PAs had shown some interesting gas permeation properties, they were not explored much as a membrane material for gas separation applications [9,10], due to their insolubility, processing difficulty and low gas permeability. The rigid backbone and strong interchain hydrogen bonding which result in high cohesive energy density and dense chain packing are behind these anomalies [10]. Improved solubility of the polyamides is sought to allow the preparation of membranes for these high end applications. To overcome such difficulty and to achieve required property, polymer-structure modification becomes necessary. There are several approaches that have been adopted to reduce the hydrogen bonding and to restrict their close packing. It is reported in several literatures that the introduction of bulky, packing-disruptive, propeller shaped triphenylamine (TPA) groups into the polyamide backbone not only increases the

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solubility and processability of the polymers by reducing the close packing and hydrogen bonding but also helps in maintaining their high thermal and mechanical property [11,12].

TPA containing polymers showed interesting gas separation behavior [1,11,13,14]. Hu et al. prepared multifunctional TPA containing polyimides with pendant anthraquinone moiety and reported enhanced CO<sub>2</sub> permeability [1]. Chang et al. reported improvement of gas permeability with decrease in gas selectivity for polyimides containing different methoxy substituted TPA units [11]. Li et al. studied the gas permeation properties of the polyimides containing p-tertbutyl substituted TPA and reported improvement in the O<sub>2</sub>, CO<sub>2</sub> permeability with little decrease in selectivity compared to their unsubstituted analog [13]. Yen et al. synthesized polyimides with trimethyl substituted TPA and reported higher permeability and selectivity for CO<sub>2</sub>/CH<sub>4</sub> gas pair [14]. It is known that the presence of the trifluoromethyl groups in polymer repeat units improves many of polymer properties and enhances the polymer solubility and gas permeability [8–10,15]. However, the high production cost of the fluorinated monomers and associated environmental issues with fluorine, the nonfluorinated polymers, may be of better choice. In our previous work, we have reported the gas permeability of a series of PAs prepared from a flexible diamine containing bulky adamantane moiety. The reported PAs showed high permselectivity (for, O<sub>2</sub>/N<sub>2</sub> ~ 8.2 and for CO<sub>2</sub>/CH<sub>4</sub> ~ 41.7) with moderate permeability [9]. In continuation of our work to improve the gas permeability as well as selectivity in the present work we intend to simultaneously increase the rigidity and interchain spacing (i.e., fractional free volume) by developing a new diamine monomer containing propeller shaped TPA moiety.

In the quest of developing a nonfluorinated monomer considering the economic aspect of the membrane based gas separation, we have designed and prepared a new non-fluorinated diamine monomer namely, 4-(1'-adamantanemethoxy)-4',4''-diaminotriphenylamine. This diamine monomer was successfully utilized to prepare a series of new polyamides (PAs). This work focused on the preparation of a new series of PAs with 1-adamantanemethoxy substituted triphenylamine (TPA), their detailed characterization, investigation of thermal, mechanical and dielectric properties including gas

separation properties. We also performed the computational molecular dynamics simulation to understand the gas transport properties of the PAs.

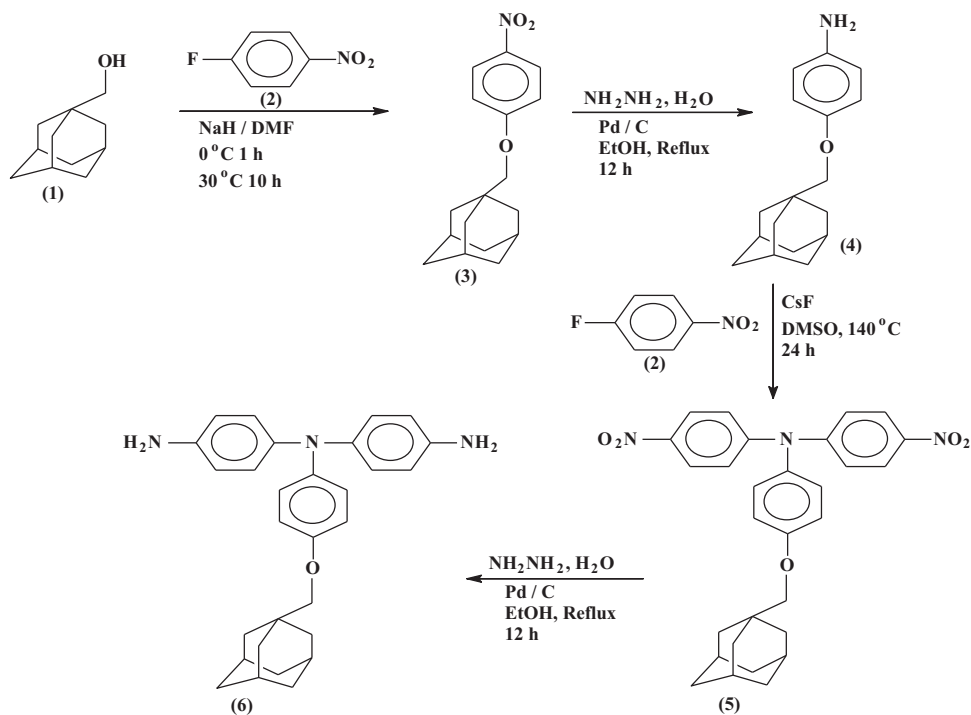
## 2. Experimental section

### 2.1. Starting materials

1-Adamantanemethanol, sodium hydride, palladium on activated carbon (1 wt%), triphenyl phosphite, 4,4'-(hexafluoroisopropylidene) bis(benzoic acid), 5-tert-butylisophthalic acid, isophthalic acid, terephthalic acid, 2,6-naphthalenedicarboxylic acid, and 1-fluoro-4-nitrobenzene were purchased from Sigma Aldrich and used as received. Cesium fluoride was purchased from Sigma Aldrich and dried for 6 h at 160 °C before use. N,N-Dimethylacetamide (DMAc), and tetrahydrofuran (THF) were used as received from Merck. N,N-Dimethylformamide (DMF) (Merck) was distilled from P<sub>2</sub>O<sub>5</sub> prior to use. Dimethyl sulfoxide (DMSO) (Merck) was dried using calcium hydride. 1-Methyl-2-pyrrolidinone (NMP) (Merck) was purified by stirring with NaOH and distilled from P<sub>2</sub>O<sub>5</sub> prior to use. Toluene (Merck) was dried by refluxing over sodium metal. Pyridine (Merck) was purified by stirring with NaOH and distilled under reduced pressure. CaCl<sub>2</sub> (Merck) and anhydrous K<sub>2</sub>CO<sub>3</sub> (Merck) were dried for 12 h at 140 °C before use. Methanol (Rankem) was used for precipitation of polymers. The synthesis of the new diamine (6) is depicted in Scheme 1. Detailed preparation of the diamine monomer is given in the Supporting information (SI).

### 2.2. Equipment

Carbon, hydrogen and nitrogen contents of the compounds were determined using a Vario EL (Elementar, Germany) elemental analyzer. FTIR spectra of the monomers and polymers were recorded using a NEXUS 870 FTIR (Thermo Nicolet) spectrophotometer at room temperature using KBr pellets. <sup>1</sup>H NMR spectra were recorded on a Bruker 400 MHz instrument (Switzerland) using DMSO-d<sub>6</sub>, and pyridine-d<sub>5</sub> as solvents. Gel permeation chromatography (GPC) was



Scheme 1. Synthesis of the diamine monomer '6'.

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