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# Polyaniline/polybenzimidazole blends: Characterisation of its physico-chemical properties and gas separation behaviour

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ABSTRACT

Novel polymer blends were prepared by casting blend solutions of polyaniline (PANI) and polybenzimidazole (PBI) at various ratios. Prepared blends were amorphous and had good film homogeneity without defects. From mechanical analysis it was found that tensile strength diminishes with increasing content of PANI. WAXS analysis disclosed the amorphous structure of PANI/PBI blends. IR spectra indicate clearly the presence of PANI in PBI matrix and NMR spectra revealed significant interactions of PBI with PANI. Permeability, diffusion, solubility coefficients and sorption capacities of all measured gases ($H_2$, $O_2$, $CH_4$, $N_2$, $CO_2$ and water vapour) decreased with increasing PANI content whereas ideal selectivities increased for all observed gas pairs. Doping of blends with hydrochloric acid led to a significant decrease in permeabilities and sorption capacities while selectivities slightly increased.



## 1. Introduction

Membrane technology arouses great interest in the industry, due to the numerous advantages over other separation processes, e.g. ease of operation, high reliability, low energy requirements, compact size, and environmental friendliness [1,2]. The choice of a membrane material for gas separation applications is based on specific physical and chemical properties and therefore it is desirable that these materials could be tailored to meet the requirements efficiently.

The past decade was marked by the appearance of a number of novel interesting membrane materials, such as zeolites, silica, metal organic frameworks (MOFs), graphene-based materials, organic–inorganic hybrid materials, high-performance polyimides, thermal rearranged (TR) polymers, polymers of intrinsic microporosity (PIMs), ionic liquids (ILs), and perfluoropolymers [3–7]. Although hundreds of inorganic and polymeric membranes have been investigated so far, only several ones are applied in gas separating plants. Up to now, extensive research has been conducted on polymer membranes [7–11], however their performance is circumscribed by a trade-off between permeability and selectivity [12], wherefore researchers explored the concept of polymer blending.

Polymer blends have scores of advantages over those of a single polymer. It is a time- and cost-effective method to combine the advantages of several polymers to obtain new materials with superior properties and hence durable membranes with enhanced gas separation performance. To date, several types of blend membranes for gas separation have been reported [13–17].

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A special group of blend membranes comprises intrinsically conducting polymers, such as polyaniline (PANI) [18–22]. PANI arouse great excitement in the centre of scientist's attention due to its ease of synthesis, unique electrical properties and its numerous potential applications [23,24]. Due to its distinctive features, PANI has been extensively studied as a potential membrane material. Anderson et al. reported remarkable selectivity values of various gas pairs for a series of PANI films, e.g. 3590 for $H_2/N_2$, 30 for $O_2/N_2$, and 336 for $CO_2/CH_4$ [25]. Su and his group performed gas permeability tests with blended films made from polyaniline and polyimide. They observed that the blend has a greater gas selectivity and shows an increase in permeability for all studied gases in comparison to neat polyimide [26]. Besides, simple acid/base doping/undoping enables to enhance membrane performance, which was confirmed by works of Kuwabata et al. It was found that $O_2/N_2$ selectivity increases with doping level from 9.5 (undoped) to 14.9 (36% doped) to 15.2 (50% doped) [27].

As all these studies indicate, polyaniline is an interesting candidate for new materials with tailorable properties. However, further investigations are required for the future use as membrane material for gas separation, because PANI possess insufficient film-forming properties and inadequate mechanical properties. To overcome these problems, various approaches have been tried, e.g. deposition of a thin layer on a support material [28] or polymer blending [26]. Hence, PANI was combined with another conventional polymer polybenzimidazole (PBI), that possess similar molecular structure like polyaniline which seems to be promising for preparation of a polymer blend. PBI is known to be a temperature stable polymer with high mechanical stability [29]. Besides, it is a selective polymer with desirable inherent gas transport properties. Its excellent film forming properties removes the brittleness and lack of processibility of PANI; thus facilitates the preparation of a stable polymer film with PANI.

Based on this context, this work focuses on the influence of PANI on physico-chemical properties of the polymer blend and aims to investigate the effect of PANI content and doping of the blend on gas transport properties. It is expected through the addition of PANI that the selectivities will increase, because PANI is less permeable than PBI. By adding dopant, we assume changes in the chemical structure and morphology, e.g. decrease of the *d*-spacing of PANI film [22], and thus an increase of ideal selectivities to a higher factor.

## 2. Experimental

### 2.1. Materials

Polybenzimidazole (PBI), full chemical name poly(5,5-bibenzimidazole-2,2-diyl-1,3-phenylene) (Hoechst Celanese), was used as received as a 10% N,N-dimethylacetamide (DMAc) solution with a lithium chloride content of ~2%.

Polyaniline (PANI) is a conducting polymer and can be found in one of three idealized oxidation states: (1) Leucoemeraldine, (2) Emeraldine and (3) Pernigraniline. In the present case, PANI (Emeraldine) was synthesized by the method of Stejskal and Gilbert [30] via oxidative polymerization of aniline hydrochloride (Sigma–Aldrich) with ammonium peroxodisulfate (Lach-Ner). The resulting product is PANI Emeraldine salt (PANI salt). The resulting PANI salt was neutralised in 0.1 M ammonium hydroxide overnight to obtain the PANI Emeraldine base (PANI base). Afterwards, PANI base was washed with acetone, and in the end dried at room temperature for 24 h. In Fig. 1 is presented the reaction scheme of PANI synthesis.

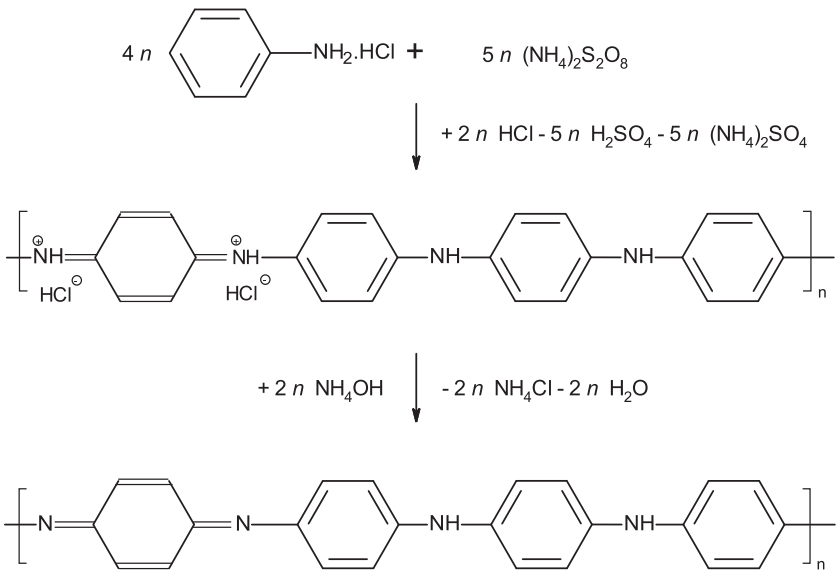


**Fig. 1.** Synthesis of PANI salt [26] and conversion to PANI base.