Mechanically and Thermally Enhanced Intrinsically Dopable Polyimide Membrane with Advanced Gas Separation Capabilities

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Introduction

In this paper, we present the first preparation of an intrinsically dopable polyimide (DPI) membrane containing an amine-capped aniline trimer (ACAT) that reveals advanced gas separation capabilities as well as mechanically and thermally enhanced properties. The as-prepared DPI membrane was synthesized by reacting ACAT and 4,4o-(4,4o-isopropylidenediphenoxy)bis(phthalic anhydride) (BSAA) through a conventional thermal imidization reaction. Polyaniline (PANI) and conventional nondopable polyimide (NDPI) membranes were also prepared as controls. The DPI membranes were found to reveal permselectivities (R) ofO_2/N_2 of about 13.54, which is about 1.96- and 1.54-fold higher than that of NDPI and PANI, respectively, based on the investigation of gas permeability analysis (GPA). Upon doping with 1.0MHCl (aq), the pemselectivities of DPI for O_2/N_2 were found to be further increased to about 16.63. Moreover, significantly enhanced mechanical and thermal properties of the as-prepared DPI membrane were also found as compared to those of NDPI and PANI membranes, based on the studies of dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), respectively.

Results and Discussion

The permeability coefficients of O_2, N_2, and CO_2 for DPI, NDPI, and PANI membranes were investigated by performing permeation tests at different operational temperatures, as shown in Figure 7 and listed in S-Table 1 (see Supporting Information). The permeability coefficients of corresponding samples for three gases decreased at each temperature, in the order $P(CO_2) > P(O_2) > P(N_2)$. This was also the order of increasing kinetic molecular diameters (CO_2, 3.30 Å;O_2, 3.46 Å; andN_2, 3.64 Å) of the penetrant gases. It was observed that the permeability of NDPI and DPI was higher than that of PANI. Generally speaking, chemical structures coupled with subtle physical properties of the membrane material could influence the permeability and selectivity of a gas. The responses of a polymeric material to permeation are strongly influenced by the polarity and steric characteristics of both the polymer and permeate. The size and shape of bulky groups in both polymer backbones and side chains determine certain fundamental properties like packing density and rigidity, which in turn influence permeability. These parameters, along with the diffusion coefficient, govern the separating capabilities of polymers for O_2, N_2, and CO_2 gas pairs. As polymer molecular spacing becomes tighter the permeability decreases due to decreasing diffusion coefficients but the separation characteristics are enhanced. In this work, polyimide systems contained either rigid (ODA or ACAT) or flexible blocks (BSAA). Rigid block segments provided the main structural framework and better thermal resistance, while the flexible block governed the transportation of gas molecules. On the other hand, PANI consisting of a fully rigid aromatic structure has a higher packing density than polyimide systems. After doping protonic dopants (e.g., 1.0 M HCl) to imide nitrogen on either PANI or DPI backbones, the permeability decreased for all the gases. This effect was due to doping DPI or PANI, in which the dopant reduced the free volume in the polymer (morphological changes) and led to an obvious decrease in gas permeability.

Conclusions

In conclusion, we present the first preparation of an intrinsically dopable polyimide (DPI) membrane containing an amine-capped aniline trimer (ACAT) that reveals advanced gas separation capabilities as well as mechanically and thermally enhanced properties. In regard to gas separation, the permeability and permselectivity of the DPI membrane can be tuned by doping with a dopant. This doping behavior is similar to PANI. Compared with a conventional nondopable PI (NDPI) and PANI, the DPI has good permselectivity about 1.5-fold higher than PANI and 2-fold higher than NDPI. Upon doping with 1.0MHCl (aq), the permselectivity of DPI was about 2.4-fold higher than that of NDPI. In regard to physical properties, DPI has excellent thermal stability and mechanical properties similar to NDPI. Comparing the mechanical properties of the NDPI and PANI membranes, the DPI membrane showed a storage modulus of 2800 MPa at 30℃, which was an increase of about 39.4% and 55.5% higher than that of NDPI and PANI membranes, respectively. The decomposed temperature of DPI also increased substantially, to around 131 ℃ as compared with PANI and to around 46℃ as compared with NDPI. The DPI has good thermal stability, mechanical properties, and high permselectivity,

Reference

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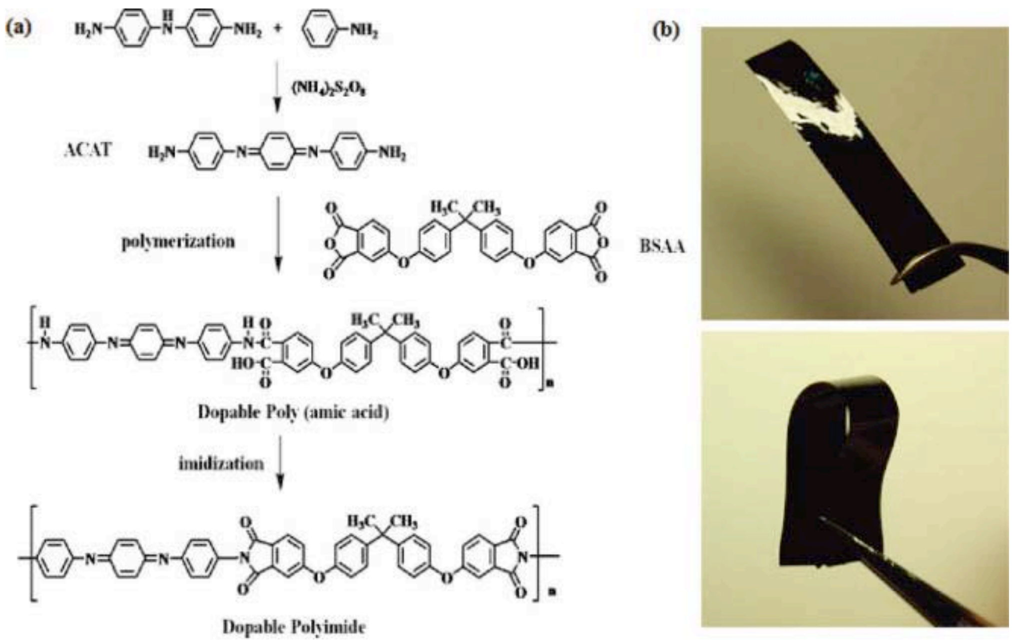

Figure 1. (a) Schematic representation of the synthesis of ACAT and dopable polyimide (DPI) and (b) photographs of DPI.

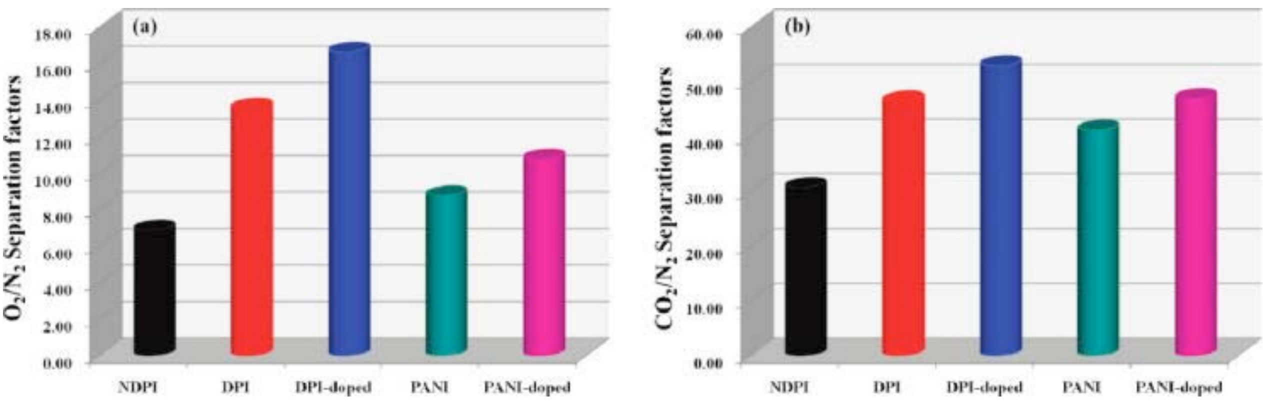

Figure 2. Variation of permeability selectivity for the studied membranes at 303 K (a) O_2/N_2 and (b) CO_2/N_2.