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Molecular Packing and Anisotropic Orientation of Tröger's Base (TB)-based Polyimide/Copolyimide Membranes

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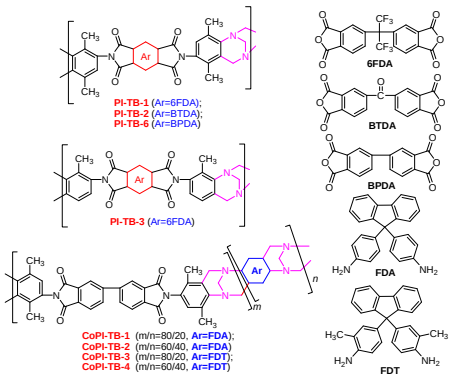
Abstract: The degrees of molecular packing (*e.g*. free volume) and orientation of main chains are key parameters for the physical properties of microporous polymers, especially for gas separation membranes. In this study, the molecular packing and orientation of several types of Tröger's base (TB)-based polyimides (PIs)/copolyimides (co-PIs) with intrinsic microporosity were probed by optical measurements and out-of-plane thermal diffusivity ($D_\perp$). The TB-based PIs/co-PIs exhibited low average refractive indices (1.529~1.606) and low-to-moderate birefringence (0.019~0.048) at 1310 nm, and low $D_\perp$ ranging from 6.2 to 8.5 $\times 10^{-8}$ m^2/s depending on the chain structures. The free volume fractions within membranes were also estimated based on the Lorentz-Lorenz equation combined with semi-empirical AM1 calculations of molecular polarizability. The related properties such as dielectric constants and thermal expansion behaviors are also investigated to probe the correlation between the structures and properties of TB-based PIs/co-PIs.

Keyword: polyimides; polymers of intrinsic microporosity; molecular packing; orientation; Tröger's Base

Introduction: Polymers of intrinsic microporosity (PIMs) can behave like molecular sieves in the solid state for the applications in gas separation due to the combination of microporosity and high free volume fraction.[1-3] The free volume of polymer membranes can be estimated by experimental density, positron annihilation lifetime spectroscopy (PALS)[4], and ^{129}Xe NMR spectroscopy.[4-6] However, these methods have more or less certain limitations, especially for very thin membranes and high free volume membranes such as PIMs. Moreover, chain orientation in membranes is important for obtaining optimized properties such as mechanical, optical, and electrical properties as well as thermal expansion behaviors under harsh application conditions. To our best knowledge, no related research has been performed to investigate the degrees of chain orientation of PIM-PIs. Recently, a rigid, bridged, and V-shaped bicyclic 1,5-methano-1,5-diazocine (Tröger's base, TB) has been effectively incorporated into the backbone of PIMs to produce highly permeable molecular sieve membranes (*e.g*., PIM-EA-TB)[1], and novel PIM-PIs based on the TB units have been explored.[7-9] The detailed properties of TB-based PI/co-PI membranes for gas separation applications such as mechanical, thermal and gas separation properties have been investigated.[7-9] In this study, we focus on the evaluation of the free volume fractions and anisotropic orientations for a series of TB-based PIs/co-PIs membranes (shown in **Scheme 1**) based on refractive index, thermal expansion, and thermal conductivity measurements combined with semi-empirical AM1 calculations of linear polarizability. The related properties such as dielectric constants, thermal behaviors, and out-of-plane thermal diffusivity coefficients, are also investigated to probe the correlation between the structures and properties.



Scheme 1. Chain structures of TB-based polyimides/co-polyimides

Experiments and theoretical basis: A series of Tröger's base-based PIs/Co-PIs were synthesized by the procedures previously reported.[7-9] The polymer powders were dissolved into NMP to form the corresponding polymer solutions with a 5% solid concentration. The 6~10 μm-thick membranes were prepared by coating polymer solutions onto Si substrates followed by evaporating NMP solvent by successive heating at 60 °C/5h, 120 °C/2h and 220 °C/3h in a vacuum oven. For the estimation of their free volume fraction (*FFV*, V_f), the degree of chain packing (K_p) were estimated based on eq. (1)[10,11] where V_w is the van der Waals molar volume based on Bondi's group contribution theory, cm^3/mol; n_{av} and α_{av} are the average refractive index and the average molecular polarizability, respectively.[10] Furthermore, based on the calculated K_p values, the free volume fraction (*FFV*, V_f) can be estimated by the eq. (2).

$$K_p = \left(\frac{n_{av}^2 - 1}{n_{av}^2 + 2}\right) \cdot \frac{3}{4\pi} \cdot \frac{V_w}{N_A \cdot \alpha_{av}} \quad (1)$$

$$V_f = \frac{V - 1.3V_w}{V} = 1 - 1.3K_p \quad (2)$$

Table 1. Physical properties of TB-based polyimides/co-polyimides

sample	n_{av} [a]	Δn [b]	α_{av} [c] (Å)	V_w [d] (cm^3/mol)	V_f	$D_\perp$ [e] ($\times 10^{-8}$ m^2/s)	$\Phi_\perp$ [f]	ε_{opt} [g]	CTE (ppm/K)
PI-TB-1	1.529	0.0190	69.2	340.4	0.218	6.2	0.289	2.57	52.6
PI-TB-2	1.596	0.0257	65.3	302.3	0.188	8.5	0.320	2.80	48.5
PI-TB-3	1.546	0.0257	65.3	320.8	0.198	6.5	0.299	2.63	44.0
PI-TB-6	1.606	0.0481	63.3	291.0	0.183	7.2	0.318	2.84	31.2
CoPI-TB-1	1.606	0.0406	60.2	273.9	0.192	7.1	0.319	2.84	32.8
CoPI-TB-2	1.606	0.0304	57.2	256.8	0.202	7.0	0.319	2.84	39.7
CoPI-TB-3	1.600	0.0396	61.0	277.8	0.197	6.8	0.317	2.82	36.3
CoPI-TB-4	1.594	0.0307	58.8	264.7	0.212	6.9	0.315	2.79	42.3

[a]Average refractive indices (1310 nm); [b]In-plane/out-of-plane birefringences (1310 nm); [c]Molecular polarizabilities calculated by semi-empirical AM1 in VAMP model in Materials studio 7.0; [d]Van der waals molar volume; [e]Out-of-plane thermal diffusive coefficients; [f]Vuks parameter; [g]Out-of-plane thermal diffusivities; [h]$\varepsilon_{opt}=1.1\ n_{av}^2$.

Results and discussion: As listed in **Table 1**, the TB-based PIs/co-PIs membranes exhibited relatively low n_{av} (1.529~1.606) and low-to-moderate birefringences (n, 0.019~0.047) at 1310 nm. The estimated free volume fractions (V_f) within membranes varied from 0.192 to 0.218, which is very close to those estimated from density measurements. In addition, the order of V_f is similar to that of their CO_2 permeability as shown in **Fig. 1**, indicating the free volume fraction mainly controls the CO_2 permeation within the TB-based PI/co-PI membranes. Moreover, the optically estimated dielectric constants (ε) of the TB-based PIs/Co-PIs were smaller than 2.90, indicating their good dielectric properties as insulators in electronic applications.

These TB-based PIs/Co-PIs exhibited low to moderate in-plane CTE values within 31.2~52.6 ppm/K, depending on the chain structures. Similar to conventional PI films, their linear thermal expansion behaviors are also closely related to the degrees of in-plane orientation of main chains as shown in **Fig. 2**.

Moreover, these TB-based PIs/Co-PIs exhibited $D_\perp$ values of smaller than 8.5 x 10^{-8} m^2/s, which is much smaller than those of conventional PI films, such as BPDA-PDA (16.5 × 10^{-8} m^2/s) and 6FDA-ODA (12.3 × 10^{-8} m^2/s). We have reported that the $D_\perp$ showed a positive linear correlation with modified Vuks parameters $\Phi_\perp$. The TB-based PI/Co-PI membranes presented smaller $\Phi_\perp$ values than those of the conventional PI films such as BPDA-PDA (0.3415) and 6FDA-ODA (0.3206), which agrees well with their smaller $D_\perp$ values.

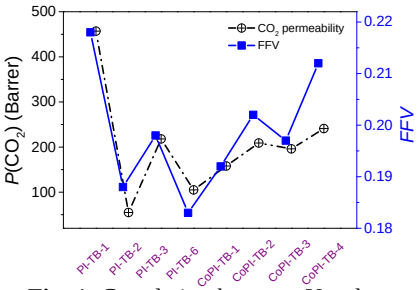


Fig. 1. Correlation between V_f values and CO_2 permeabilities of the TB-based polyimides/co-polyimides.

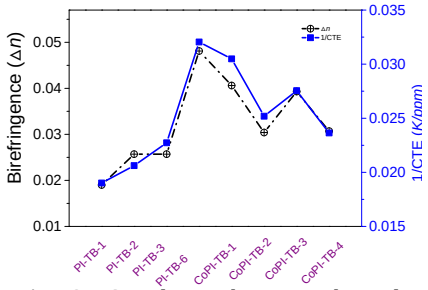


Fig. 2. Correlation between thermal expansion coefficients (CTE) and birefringence (Δn) of TB-based polyimides/co-polyimides.

Conclusions: The molecular packing and in-plane chain orientation of several types of TB-based PIs/Co-PIs were quantitatively estimated by optical measurements and out-of-plane thermal diffusivity. The TB-based PIs/Co-PIs exhibited low average refractive indices (1.529~1.606), low-to-moderate birefringences (0.019~0.047) at 1310 nm, and $D_\perp$ values smaller than 8.5 × 10^{-8} m^2/s depending on the chain structures. The estimated free volume fractions (V_f) within membranes varied from 0.192 to 0.218. In addition, their dielectric constants (ε) were smaller than 2.90 based on refractive index measurements. These properties, which are explainable by the molecular packing and orientation parameters, are suitable for electronic and optical applications.

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