# TRÖGER'S BASE (TB)-BASED POLYIMIDE/COPOLYIMIDE MEMBRANES: FREE VOLUME AND CHAIN ORIENTATION

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Polymers of intrinsic microporosity(PIMs) have presented various applications for gas separation, gas storage, heterogeneous catalysis, and adsorption, sensorsdue to their overall performance advantages, especially in combination of solution processability and microporosity.[1-3] Toward the separation applications, free volume is very important to understand the gas transport for membrane materials. For example, the amounts of free volume directly determine the gas diffusions and play an important role on gas permeations. The free volume of polymer membranes can be estimated by experimental density, positron annihilation lifetime spectroscopy (PALS) measurements[4] and $^{129}$Xe NMR spectroscopy[4-6]. However, these estimation methods more or less present some certain limitations. As for the density measurements, significant discrepancy frequently presents due to the large experimental errors, especially for thin membranes (e.g., less than 10 μm-thick) and high free volume polymers, such as PIMs including PIM-polyimides (PIM-PIs)having strong adsorption characteristics.[7] It is worth to note that another method for the estimation of the degree of chain packing ($K_p$) based on the modified Lorentz-Lorenz equation has been proposed by our group.[8, 9] This method requires only experimental refractive indices and calculated molecular polarizability tensors.[8] Moreover, the control of chain orientation in membranes is important for obtaining optimized properties such as mechanical, optical, and electrical properties as well as thermal expansion behaviors. It is well known that the main chains of typical PIMs as well asPIM-PIs are very rigid (*e.g.* ladder polymer chains), the introduction of sites of contortion (*e.g.* spiro-centres) into the chain backbone should results in different orientation behaviors from the common dense membranes. To our best knowledge, no related research has been performed to investigate the degrees of chain orientation of PIM-PIs.

Recently, rigid, bridged, 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) by Mckeown et al.[1],and PIM-PIs based on TB units have been explored by Leeet al.[10-12] 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 in detail.[10-12]Here, we willfocus on the evaluation of the free volume and anistropic orientation for a series of Tröger's Base (TB)-based PIs/co-PIs membranes based on optical birefringence measurements, thermal expansion,and thermal conductivity charaterizations combined with semi-empirical AM1 calculations for molecular polarizability.The membranes exhibited low average refractive indices (1.52~1.61) and low-to-moderate birefringences (0.019~0.047) at 1310 nm. The estimated free volume fractions within membranes varied from 0.196 to 0.221. The related properties such as dielectric constants, thermal behaviors, and out-of-plane thermal diffusivity coefficients, arealso investigated to probe the correlation between the structures and properties.

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**References**

1. M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J. C. Jansen, P. Bernardo, F. Bazzarelli and N. B. McKeown, *Science*, **2013**, *339*, 303-307.
2. M. D. Guiver and Y. M. Lee, *Science*, **2013**, *339*, 284-285.
3. N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, **2006**, *35*, 675-683.
4. B. Nagasaka, T. Eguchi, H. Nakayama, N. Nakamura and Y. Ito, *Radiat. Phys. Chem.*, **2000**, *58*, 581-585.
5. T. C. Merkel, L. G. Toy, A. L. Andrady, H. Gracz and E. O. Stejskal, *Macromolecules*, **2003**, *36*, 353-358.
6. T. Miyoshi, K. Takegoshi and T. Terao, *Polymer*, **1997**, *38*, 5475-5480.
7. A. V. Maffei, P. M. Budd and N. B. McKeown, *Langmuir*, **2006**, *22*, 4225-4229.
8. Y. Terui and S. Ando, *J. Poly. Sci., Part B: Polym. Phys.*, **2004**, *42*, 2354-2366.
9. D. Yorifuji and S. Ando, *Macromolecules*, **2010**, *43*, 7583-7593.
10. Y. Zhuang, J. G. Seong, Y. S. Do, H. J. Jo, Z. Cui, J. Lee, Y. M. Lee and M. D. Guiver, *Macromolecules*, **2014**, *47*, 3254-3262.
11. Y. Zhuang, J. G. Seong, Y. S. Do, W. H. Lee, M. Lee, Z. Cui, A. E. Lozano, M. D. Guiver and Y. M. Lee, *Chem. Commun.*, **2016**, *52*, 3817-3820.
12. Y. Zhuang, J. G. Seong, Y. S. Do, W. H. Lee, M. J. Lee, M. D. Guiver and Y. M. Lee, *J. Membr. Sci.*, **2016**, *504*, 55-65.