Tröger's base (TB)-Based Polyimides: Synthesis, Structure-property Relationships, and Their Applications

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Tröger's base (TB) is a rigid *V*-shaped bridged linking unit, providing a highly rigid and permanently distorted position to inhibit the formation of effective interchain dense packing. A series of TB-based polyimides (PIs)/co-polyimides (co-PIs) have been synthesized *via* polymerization between imide-containing diamines and dimethoxymethane (DMM) as shown in **Fig.1**. The detailed investigation of the structure-property relationships for these PIs/co-PIs was undertaken. They had high fractional free volume (FFV ≥0.164) resulting from poor chain-packing and exhibited significant microporosity. They were readily soluble in common organic solvents, had good mechanical properties, with tensile strength in the range of 59−121 MPa and elongation at break of 5−126%, good thermal stability and extremely high glass transition temperatures (T_gs) above 395°C. Also, they exhibited relatively low average refractive indices, low-to-moderate birefringence, and ultra-low thermal conductivity (λ) values (0.035−0.145 W/mK). They exhibited low dielectric constants (D_k = 2.25−2.80) at 10 GHz. The influences of incorporating TB units into chain backbones on aggregation structures and physical properties for these TB-based PIs/co-PIs were identified. Incorporating TB units into chain backbones effectively reduced the degree of chain orientation and increased fractional free volume, leading to both low D_k and low λ values. Also, introducing TB units enhanced molecular weights, toughness, and glass transition temperature (T_g) of the resulting PIs.

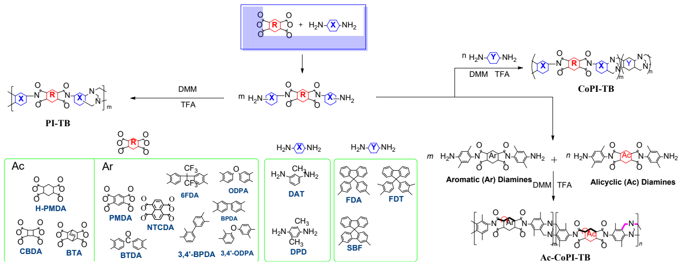

Fig.1 Monomer structures and synthetic routes of TB-based polyimides/co-polyimides.

The TB-based PIs/co-PIs have various applications due to their overall performance advantages, especially in combination of solution processability and microporosity with structural diversity. Owing to the intrinsic microporosity, the gas permeabilities of the membranes were significantly higher compared to conventional PIs. The gas separation performance (e.g., H_2/CH_4, H_2/N_2, CO_2/CH_4 and H_2/CO_2) can be significantly adjusted by incorporating deliberately chosen segments *via* copolymerization. Some partially alicyclic TB-based PIs are totally colorless and transparent with transmittances above 77% at 400 nm, and showed dual fluorescence and phosphorescence emissions at low temperatures. In addition, we constructed wide-temperature-range proton exchange membranes (PEMs) by incorporating crown ether units into chain backbones. The resulting PA-doped co-PI membrane electrode assemblies (MEAs) can easily operate stably from 30 to 160 °C under H_2/air conditions even without any external humidifiers. The single-cell based on PI-TBN30C achieved maximum power densities of 250 and 361 mW cm^{-2} at 80 and 160 °C, respectively. Their excellent overall performance highlights their potential applications in membrane-based gas separation, electrolyte membranes for fuel cells, spectral conversion of unused UV solar radiation to useful visible light, heat-insulating and low-*k* dielectric materials, etc.