Unusual Glassy Polymer Membranes for High Gas Permeation

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Molecular engineering and architecture of polymers play important roles in all their specific applications. Particularly, polymer membranes have gained an important position in chemical technology and are used in a broad range of applications such as water purification, gas separation, and fuel cells. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. In separation applications, the ultimate goal is to allow one component of a mixture to permeate preferentially through the membrane, while preventing permeation of other components. Nonporous, dense polymer membranes consist of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity (D) and solubility (S) in the membrane material. Experimental studies of better polymer membrane materials for energy-saving and environmental applications are challenging, as they still require high flux and more selective properties, as well as excellent thermal and chemical stability in some harsh conditions, as compared to other conventional separation technologies.

Up to date, aromatic polymers interconnected with heterocyclic rings (e.g., imide, benzimidazole, benzithiazole and benzoxazole) have attracted much attention owing to their excellent thermal, chemical, mechanical properties. Basic unit of phenylene-heterocyclic ring can lead to a rigid-rod or a semi-rigid structure in combination with swivel groups (e.g., ether linkage). Intrasegmental stiff and rigid units in flat topology may increase chain packing density and decrease solvent-accessible free volume, enhanced by intersegmental interactions such as a charge transfer complex between heteroatoms (e.g., O, N and S) containing lone electron pairs. In particular, polybenzoxazole (PBO) is a class of heterocyclic polymers with properties similar to polyimide (PI). They all have excellent thermal stability, high mechanical properties, and superior chemical resistance. Unlike PI, PBO does not possess polar carbonyl groups in their backbones, so they show lower water absorption and dielectric constant than polyimides. They are more suitable for use in the microelectronic industry as buffer coatings in IC chips, interlayer dielectrics for multilayer electronic devices, substrates for flexible printed circuit board and tape automatic bonding, and high and electronic packaging materials. Spurred by the need for materials resistant to high temperature and corrosive atmosphere, there polymers have attracted much attention but their applications are still limited in the membrane separation areas owing to poor solubility in common solvents.

A significant route to solve the difficult problem of fabricating these polymers is to use the concept of post-fabrication polymer-modifying reactions. Our current studies have revealed that there completely aromatic, insoluble, infusible polymers, analogs of polyphenyl, can be made only by cyclodecarboxylation at about 350-450°C on a film or fiber of an aromatic polyimides. The intermediate, soluble or insoluble polyimide of high molecular weight is prepared by the condensation of dianhydrides with aromatic diamines including *ortho*-positioned OH, NH2, and SH. These polymers are stable in air up to 450°C, resistant to attack by hot acid and bases, and partially soluble or swollen in concentrated H_2SO_4. The solid-state, post-fabrication, cyclodehydration which was involved with their respective aromatic polymers appears to be solely intramolecular and thus does not result in any significant crosslinking. More recently we have developed a keen interest in the *in situ* thermal conversion of reactive functional group-containing aromatic polyimides into rigid-rod-like or semi-ladder polymers possessing excellent mechanical, thermal, and chemical stability in various solid forms. The evidence

for this conversion process has already been presented by Kardash and Pravednikov (1). It was again confirmed by other groups. (2, 3), using large model polymers in the thermal transformation of hydroxy-containing polyimides (HPI) into polybenzoxazoles (PBO). This process represents a more favorable intramolecular reaction due to the highly restricted segmental mobility of high glass transition temperature (T_g) polyimides, accompanied by the quantitative loss of carbon dioxide after cyclization and thermal decarboxylation for T = 350–450 °C. Here we were curious about the microstructures of the resulting polymers transformed in the solid state, and assumed that the molecular structures and physical properties of this type of polymer should be very different from polymers synthesized using other common methods, even though their chemical structures were identical. This is because the molecular rearrangements can take place under highly restrained chain segmental mobility, only promoted by the external thermal energy located near to, or just above T_g, while the polymers derived from the liquid or molten state would have a more relaxed and well-packed chain structure *via* these equilibrated processes, such as slow solvent evaporation and further annealing.

Our current approach uses irreversible spatial rearrangement of disordered amorphous chain conformations in an initial solid state. Although this conversion process is applied at high temperature of 350-450 °C, it retains virgin polymer character as revealed by spectroscopic evidences. Here we demonstrate that a spatial rearrangement of disordered semi-rigid polymer chains in a confined manner can provide large amount of micropores and unusual pore formation. By adjusting the final temperature and chemical composition, we can manipulate our system near transition temperature so that such unfolded chain structures induce dramatic changes in the microscopic cavity organization of the polymer membrane. We expect that this approach, used here to probe with high molecular transport, can be applied to study a broad range of new advanced polymer membranes.

Initially, we synthesized an HPI membrane (referred to as T-1) from 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) and 2,2'-bis(3-amino-4-hydroxylphenyl) hexafluoropropane (APAF) *via* thermal imidization up to 300 °C. Further, four other HPI samples (T-2–T-5) (Fig. 1) were prepared using the same synthetic method to investigate the chemical structure-property relationships after thermal treatment. The bulky $-C^*(CF_3)_2-$ group in dianhydride or diamine contribute to the increase in the diffusion of the gas due to the increase in the free volume. In general, it is well-known that the family of polymer including $-C^*(CF_3)_2-$ group shows a helix configuration in an energy-minimization state due to twisting and bending of polymer chain at the carbon atom (C*). Packing of the polymer is difficult by helix configuration and also gas molecules cannot easily pass among the polymer chains. In this way, helix configuration works effectively for both permeability and selectivity. Since T-1 shows a larger helix than does other polymers is supposed to have higher free volume inside of the polymer structure. All the HPI films were thermally treated up to 450 °C (referred to as T'-1–T'-5) under an inert atmosphere.
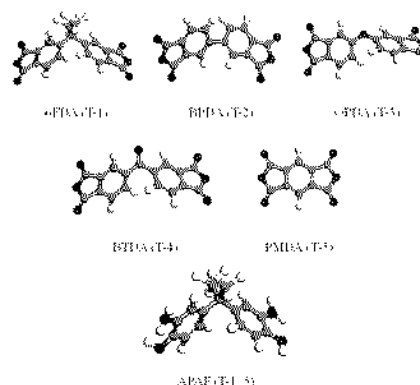

Figure 1. Chemical structures of the monomers used in this study (T-1: 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) + 2,2'-bis(3-amino-4-hydroxy phenyl) hexafluoropropane (APAF); T-2: 3,3',4,4'-bisphenyltetracarboxylic dianhydride (BPDA) + APAF; T-3: 4,4'-oxydiphthalic anhydride (OPDA) + APAF; T-4: 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) + APAF; T-5: 1,2,3,5-benzenetetracarboxylic anhydride (PMDA) +APAF)

Analysis of the mechanism of amorphous transitions in current HPIs is very important because it allows us to comprehend the nature of the genesis of unexpected microcavities in the converted polymers (i.e., PBOs) which decides their mass exchange properties. Structural disorder caused by increased asymmetric of chains also contributes to the increase of fractional free volume. These polymer chain structures from loose state to condensed state are totally amorphous, as revealed by x-ray diffraction measurement, indicating no ordered crystalline region although the PI unit chain on short range order in a segment unit includes partially regular flat-phenylene rings between interchains by dipole-dipole interactions and CTC interactions. For hydroxyl-containing PI, the dihedral angle (Φ_1) that interconnects α plane with β plane is largely distributed at around 45°±15 during NVT molecular dynamic simulation at 25 °C, and the dihedral angle distribution increases with the temperature of simulation box. That is, such segments can retain limited mobility even in the vitreous state. After a thermally-induced conversion, relatively a large flat plane (γ) is formed (here, the dihedral angle (Φ_2) is nearly close to 0° ± 5 even at an elevated temperature (450 °C).
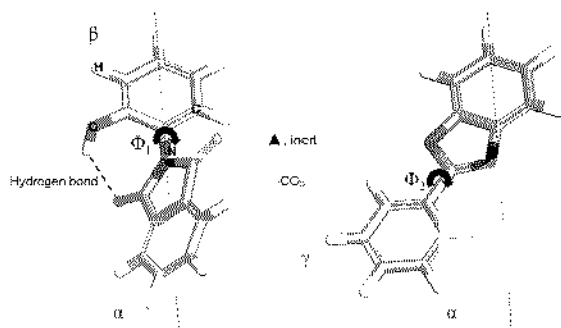

Figure 2. 3-dimensional repeating unit structure of (a) hydroxyl-containing polyimide (HPI) and (b) polybenzoxazole (PBO) derived from HPI, showing their different dihedral angles.

Noting that such a transformation occurs in a very confined solid state, so molecular defects can be formed and these microvoids play a significant role in making a space large enough to diffuse gas molecules.

Statistical mechanics and topology of a polymer chain is very enormous. The PI microstructure is in a completely amorphous state (average interchain spacing: 0.55 nm), without any crystalline domain, as revealed by x-ray scattering pattern. Molecular mechanics and dynamics simulations of the PI exhibit density (1.55 gcm^{-3}; cf. 1.58 gcm^{-3} using group contribution method) close to experimental value (1.53 gcm^{-3}). Also, x-ray pattern is very similar with real system. From these results, we assume that the simulated amorphous polymer cell would reflect the microstructure of real system. The actual rotational distribution of the dihedral angle occurs near to 45° (-135°) using the same polymer cell and its canonical ensemble (NVT) dynamics at simulation temperature range 25-450 °C for 1 ns. The reduced rotational barrier energy at higher temperature can increase the frequency of rearrangement reaction. However, the conversion efficiency would be limited by the original chain structure of PI, since this reaction occurs in a very confined space (solid state). Depending upon an initial microstructure of the polymer precursor, converted polymer chains are supposed to have a random distribution of m-m, p-p, and m-p (=p-m) (*cis* and *trans*) within a single chain if neither conformation is statistically favored (Scheme 1).
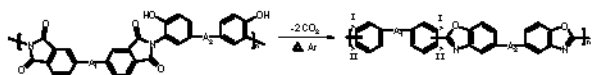
Scheme 1. A proposed reaction mechanism for the thermal conversion of hydroxy-containing polyimides to polybenzoxazoles, (I) = *para*-linked sites and (II) = *meta*-linked site

At present, from our simulation results where each amorphous cell had a different density and free volume, we believe that a random assemblage of the above chain conformations would pack poorly, leaving micropores from heavy chain disruption. The above scenario can be comprehended better, if one imagines it being like a collection of mixed strong steel wires (not an easily relaxed structure) having different geometries (i.e., zigzag-, coil-, and linear-shaped).

Positron annihilation lifetime spectroscopy (PALS) can be used to estimate the micropore size and number changes during the intramolecular rearrangement. PALS studies of the membranes suggest that initial conformation dependent microporous character, from imide ring and heterocyclic ring, reconstituted into surrounding rigid polymer chains show a change of 120% in free volume, such a large change inconsistent with common belief that chain packing density should increase due to structural relaxation at temperature around a glass transition temperature. It can be concluded that the mean size of the larger free volume cavities is increasing significantly with increasing heat treatment temperature. Differing from flexible amorphous polymers, the experimental data are indicative of a developed system of interconnected microcavities existing in the current polymers. Although the unusual pore formation is apparent at an early stage of the structure development, the actual mechanism leading to the final structuring is as yet not clear. Some of our observations suggest that intermediate pore size and shape between common glassy polymer and inorganic materials is necessary for porous structure evolution and that by-product gas diffusion plays on role in this phenomenon. The network of interconnected microcavities apparently has the widest openings compared to the other glassy polymers. Also the micropores are likely to be of the 'dumbbell-type' or 'throat and cavity' type, where a longer cavity may possess several throats. We assume that fast gas transport is required for one-directional pore growth and outstanding permselectivity represents the existence of bottleneck for sieving mechanism.

These peculiar microporous characters lead to interesting gas and ion transport. It is indicative of unique microporous structure to compare current polymer (i.e., T'-1) with a polymer having identical chemical structure (only *p-p* conformation) (4), synthesized from a usual polycondensation method. In addition, it is very interesting to compare the densities of two polymers – the polymer prepared from typical polymerization has 1.461 gcm^{-3} (4) while the density of current polymer is 1.293 gcm^{-3}, indicating the existence of large microporous character. H_2, CO_2, O_2, N_2 and CH_4 permeabilities increase 37-, 69-, 67-, 82- and 94-fold while H_2/CH_4, CO_2/CH_4 and O_2/N_2 permselectivities decrease only 0.2-, 0.7- and 0.8-fold. After rearrangement, local segmental mobility may be reduced to be stiffer owing to structural change to rigid-rod benzoxazole, as revealed by molecular modeling. As demonstrated so far, current polymers have excellent thermal stability, chemical stability and gas permeation properties. The developed polymers are one of good candidate for tailor-made microporous structure to achieve a goal of future membrane devices.

References

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