고투과성 고분자막의 신규 제조방법 및 기체분리특성

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Novel Preparation Method for High Gas Permeable Polymer Membranes and Their Gas Separation Properties

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All polymeric membranes have permeable and selective properties to gas molecules, as revealed by pioneers like Graham [1]. In the field of membrane-based gas separation, it is no doubt that an ultimate goal is to develop ideal materials having high permeability and selectivity for gas mixtures such as H_2/CO_2, O_2/N_2, CO_2/N_2 and CO_2/CH_4. From many efforts, advanced polymeric materials and epoch-making membrane formation methods [2] have emerged and put the spurs to more realization of membrane-based gas separation. However, seemingly, the performance of polymeric membranes for gas separation will be rarely or slowly improved even in the future. This prospect, unfortunately, arises from a common belief based on database of previous studies [3] and theoretical backgrounds [4].

In this study, a special attention was paid to high performance homopolymers and copolymers possessing excellent thermal and chemical stability, partially rigid rod structure, and high free volume. So we designed three kinds of functionalized polyimides like Fig. 1. These polymers have functionalized hydroxyl, amino, thiazol groups and easily made from two-step thermal imidization process. These polymers were thermally converted to polybenzoxazole, polyimidazopyrrolone, polybenzthiazole by heating the films under an Ar flow in a quartz tube furnace supported on an alumina holder plate.

The final heat treatment temperature was 450 °C and the duration time was an hour. Finally we can get thermally converted polymeric films. Chemical structures after thermal conversion are shown in Fig. 2.

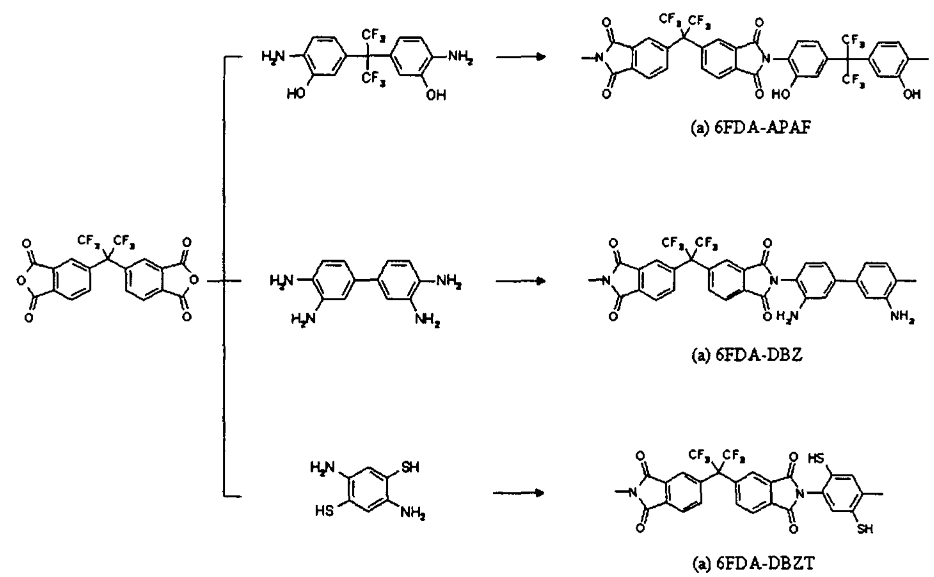

Fig. 1. Chemical structure of functionalized polyimides (a) 6FDA-APAF, (b) 6FDA-DBZ, (c) 6FDA-DBZT

Characterization of these polymers made by thermal treatment was carried out using Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis mass spectroscopy (TGA-MS), wide-angle X-ray diffraction (WAXD), and Brunauer-Emmett-Teller (BET) measurements.

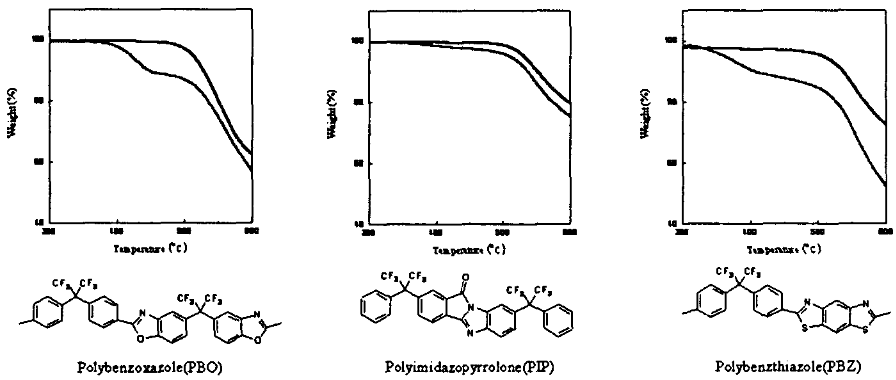

Fig. 2. TGA thermograms and their chemical structures

Fig. 2. showed the TGA thermogram of PBO, PIP, PBZ. The weight loss was observed between 350 °C and 500 °C, and this weight loss was caused by CO_2 evolution during the thermal transformation of polymer main-chain. The gas permeation experiment was carried out using time-lag method. the results are listed in Table 1. and Fig. 3. After thermal treatment, the O_2 permeability increased but O_2/N_2 selectivity decreased.

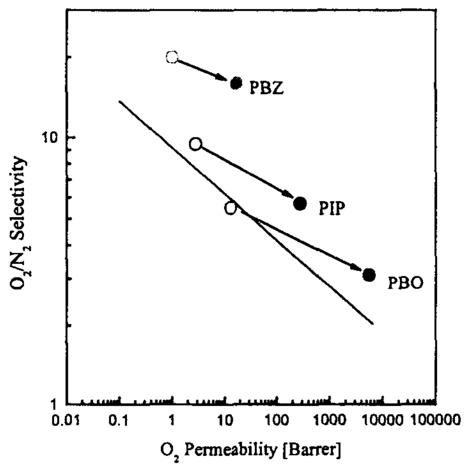

Fig. 3. The O_2 permeability and O_2/N_2 selectivity of PBO, PIP, and PBZ

High performance polymers were designed in order to create accessible free volume and can be readily prepared from simple starting materials and simple thermal treatment. The new method to obtain high permeable organic polymers will cover the field of possible applications such as adsorption, catalysis and gas separation process, even under harsh conditions because of their superior stability in the presence of organic vapours or solvents. and higher thermal stability.

Acknowledgement

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References

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