Preparation of Soluble Polyimides and Ultrafiltration Membrane Performances

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1. Introduction

In recent years, membrane processes have been used in a wide range of applications and the number of such applications have been still growing.[1-3] Ultrafiltration (UF) membrane materials, including cellulose acetate etc., cannot be used for organic solutions because of their poor chemical instabilities.[4, 5] Furthermore, commercially available UF membranes made of organic polymers are limited to operating temperatures at above 100℃. Even at below this temperature, their lifetimes are often short. There is a need to endure at harsh conditions, including crude oil separation[6], recycling of hot waters, soybian oil separation[7], etc. As a suitable material to overcome these drawbacks, polyimide, with an excellent thermal stability combined with good chemical stability and mechanical stability, is a suitable one. However, the major limitations of aromatic polyimides for the membrane applications are their high melting points and poor solubility in organic solvents.[8, 9] Although preparing polyimide membranes with poly (amic acid) is possible, complexity and uncontrollable fabrication dont make them applicable. Therefore, it is a need to prepare an asymmetric UF membrane by convenient and economical phase inversion process.

In this article, we describe the synthesis and characterization of soluble aromatic polyimides. Furthermore, with these soluble polymers, asymmetric UF membranes by the phase inversion method will be prepared and characterized.

2. Experimental

Materials: Bis[4-(3-aminophenoxy)phenyl]sulfone(BAPS-m); 4,4-oxydiphthalic anhydride(ODPA, PI-b); pyromellitic dianhydride(PMDA, PI-a); 3,3,4,4-diphenylsulfonetetracarboxylic dianhydride(DSDA, PI-c); N-methyl-2-pyrrolidone

Polymer Synthesis: Polyimide was prepared from the traditional chemical method; BAPS-m was completely dissolved in NMP and then dianhydride was precisely added at a 1 : 1 molar ratio in three portions within 30min. The reaction was carried out overnight at room temperature under a nitrogen atmosphere. A mixture of acetic

anhydride and pyridine (volume ratio 2 : 1) was added slowly to the obtained poly(amic acid) and the resulting solution was held at 110℃ for 6h. The polymer solution was poured into methanol. The precipitates were filtered, washed with methanol and water, and dried at 110℃ in vacuum.

Measurements: Infrared (IR) spectra; thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen at a heating rate 20℃/min and 10℃/min, respectively; Wide angle X-ray diffraction (WAXD) with wide angle diffraction 2θ from

code	T_g(℃)	T_i(℃)[a]	T_{10}(℃)[b]	T_{max}(℃)[c]
PI-a	267	430	520	610
PI-b	255	450	560	670
PI-c	213	420	510	595

10 to 40° .

Membrane Preparation; 22% by weight of polyimide polymer was in NMP was cast onto polypropylene nonwoven fabric with a doctor knife gap 200㎛. The membrane was precipitated by immersing into a DI ice-cold water just after casting in an environment of 65±5% relative humidity, 25±1℃ and evaporation for 30sec. After 1h, the remaining solvent was completely removed from precipitated membrane by keeping in a DI water. Cross sections of the precipitated membranes were observed by using scanning electron microscopy (SEM, JSM-5410LV).

Membrane Performances; All membranes were initially subjected to a DI water of 3Kg/cm^2 for 2h before test. Operating conditions were 25℃ and 1Kg/cm^2. Poly(ethylene glycol) 20,000 was used as solutes (1000ppm) in the feed solution. The solute concentrations in the feed and the permeate were determined by high performance liquid chromatography (Waters 410) measurements.

3. Results and Discussion

Table I Thermal properties of polyimides

[a]Onset decompostion temperature; [b]10% weight loss temperature

[c]Maximum polymer decompostion temperature.

Table II The comparison of the membrane performances between three polyimides and other polymers

[a]All polyimides membranes were prepared with the casting solution consisted of 22/78 (PI/NMP).

[b]Solute rejection rate was measured with PEG 20,000.

4. Conclusions

Soluble aromatic polyimides were synthesized by the typical chemical two-step method

from BAPS-m as a diamine and PMDA, ODPA, DSDA as dianhydrides. They were soluble in polar solvents such as NMP, DMAc, DMF, and DMSO. The inherent viscosities were 0.21 to 0.27 dL/g. Their Tgs were 213 to 267C. TGA data showed that all polymers synthesized had good thermal stabilities; initial weight loss temperature were in the range of 420 to 450C. Wide angle X-ray diffraction data indicated they are all amorphous. UF polyimide membranes were successfully prepared by the traditional phase inversion method from polyimides / NMP casting solution. All membranes had excellent ultrafiltration membrane performances; high permeation rate and high solute rejection rate at PEG MW 20,000 compared to those of other polymeric membranes such as PES and PSf. The cross section view showed very thin top layer and porous sub-layer indicating very high flux.

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	PI-a[a]	PI-b	PI-c
PWF(LMH)	375	470	450
solute rejection rate(%)[b]	98	93	97

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