# 비수계용 폴리이미드 합성 및 분리막제조

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# Synthesis and Membrane Preparation of Polyimides for Non-aqueous System

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## 1. INTRODUCTION

Polyimides are one of the most important classes of the high performance polymers due to their excellent electrical, thermal, and high-temperature mechanical properties. But their uses are limited because of their poor solubility. Most polyimide derivatives are processed in the form of polyamic acids, which are subsequently converted into the imide structures.

Recently, it has been found that the soluble polyimides with large molecular weight sufficient to application. For enhancing processability, the majority of approaches have involved the following factors. 1) As much as, the separation of the imide ring along the back-bone, that is to say, reducing the density of imide ring in the repeat structure. 2) The introduction of bulky substituents along the back-bone, in order to enhance the free volume of main-chain. 3) The incorporation of flexible or thermally stable linkages in the main-chain, reducing the packing force. 4) The disruption of symmetry or recurrence regularity through copolymerization in order to reduce crystallnity.

The objectives of this investigation are the synthesis and characterization of soluble polyimides as membrane materials by the single-step polymerization and the preparation of the asymmetric polyimide membrane by using phase inversion technique. In the present study, three series of polyimide derivatives are synthesized; H series is homopolyimides, A series is prepared from single dianhydride and two diamines, B series is yielded from two dianhydrides and a diamine. The dope solution was directly prepared from the PI solution via one step polymerization from monomers.

## 2. EXPERIMENTAL

**Synthesis of Polyimides** : A four-necked flask equipped with a mechanical stirrer, a nitrogen inlet tube, thermometer, and drying tube, and charged with diamine and NMP at 20℃. Under nitrogen conditions, equivalent dianhydride was added into the flask with stirring, and the reaction mixture was kept at this condition to obtain PAA with high molecular weight. When the reaction was completed, the azeotroping agent, p-xylene, was added, and the drying tube in the flask was exchanged distilling receiver having a reflux condenser. The mixture was rapidly heated up to 180℃ and continued until no more increased viscosity in the flow of nitrogen. The water liberated by dehydrocyclization was removed and that was observed in the receiver. On completion of the reaction, the viscose polymer solution was cooled under nitrogen atmosphere and the polymer was separated by precipitation in a large quantity of methanol. The precipitate was filtered off, washed free of used solvent by repeated use of methanol, and dried in *vacuo* at 70℃.

**Preparation of PI membranes** : All the membranes were made by phase inversion technique. Fig. 1 is a schematic diagram showing a procedure for preparing the flat sheet membrane, the dope solution could be directly prepared via one-step polymerization from monomers.

The dope solution consisted of the polymer, solvent, and additive with the specific composition. Membranes were hand cast on the nonwoven poly-propylene fabric at 25℃, RH 65±2% in the thermo hydrostatic chamber. The casting thickness was in the range of 150~300μm. The casting speed was about 5 cm/sec and the solvent evaporating period before immersion into the coagulating medium was 30sec. Phase inversion was performed by immersing the cast membrane into water bath at 0~4℃ for 6 h, and then the membrane was washed with water in room temperature for 48h.

## 3. RESULTS AND DISCUSSIONS

Fig. 2 shows the viscosity of PI as the functions of reaction time and temperature in NMP. The influence of reaction temperature was worked over a temperature range from 160 to 220℃ in the one-step polymerization. The temperatures was limited to the temperature at which the homo-geneous reaction medium could be prepared and the boiling point of solvent. As a results, the viscosity values of the polymers increased as the reaction temperature increased at below the boiling temperature. Those values with reaction time increased rapidly in the first 2 h, and after that time the values slightly rose up to complete reaction. However, the values

of viscosity obviously reduced with time, when the reaction was carried out above the boiling point of solvent. As could be deduced from those results, PI could be formed almost with a quantitative molecular weight even after 2h reacting The extent of one-step polymerization significantly depended upon the solvents which might have powerful solvent action on the monomers and the polymer. Particularly, the solvent has a strong dissolving power to propagating polymer with high molecular weight. Otherwise the polymers might deposite in the reaction mixture during propagating reaction and the preparation of PI from the one-step polymerization fails. In general, it might occur that the degradation of PI derivatives at elevated temperature in a solvent of amide type such as NMP, DMAc, and et al because of acceleration of the alkaline hydrolysis of PI. Although polymer was probably susceptible to the alkaline hydrolysis of overheated solvents of amide type, the viscosity value of polymer prepared in NMP was slightly reduced.

Fig. 3 shows the influence of azeotroping agent. For enhancing the elimination of by-product from reaction zone, p-xylene as azeotroping agent was used. On the basis of what has been put forward papers, it was suggested that the complete elimination of water liberated by dehydro-cyclization reaction be necessary, and the minimum alkaline hydrolysis of PI derivatives from overheated NMP be also requisite to obtain high molecular weight polymers. From the result, the azeotroping agent might enhance the elimination of by-product, therefore, the viscosity values of polymers increased.

The solubility of PI to organic solvents are shown in Table 1. PI was dissolved well in some aprotic polar solvents. Those good solubility was advantageous in the processability of polymer and expended the practical application

Table. 2 The chemical stability of polymeric membranes were limited with respect to pH and various organic liquids. The chemical stability of PI membrane was evaluated to organic solvents. After the membrane was immersed in those solvents for 7 days then was washed several times with pure water. the PWF the SR were calculated. In the table, the PWF and the SR values are nearly unchanged among the common organic solvents, on the other hand, the value is changed drastically in pyridine and polar solvents owing to swelling and dissolving in those liquids. It means that the PI membrane show high chemical resistance in common organic solvents.

Fig. 4 The PWF and the SR of PI membrane were calculated in the

range of pH 1-13.  The membrane was immersed in the liquids with different pH. Those values are unchanged in the range of 1-12, but the values some changed above pH 13.

## 4. CONCLUSION

PI derivatives exhibited good soluble characterization in several solvents such as NMP, DMF, DMAc, nitrobenzene, and m-cresol.  The polymers prepared by the one-step polymerizations improved the solubility and processability due to avoid several side reactions in the solid-phase imidization. The soluble polymers with large molecular weight sufficient to form strong films could be produced. The azeotroping agent, p-xylene, was enhanced the elimination of by-product.

Since the PI derivatives as membrane material have a good solubility in some aprotic polar solvents without much sacrifice in thermal and chemical stability, the dope solution could be directly prepared from the PI solution via the one-step polymerization from monomers. The permeation characteristics of PI membranes could be controlled by the several factors , such as polymer concentration, membrane thickness, the amount of additive, solvent/cosolvent system, and so on.    .

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┌─────────────────────────────────────┐
│          PMDA/BAPS/NMP               │
└─────────────────────────────────────┘
                │  ← One-step
                │    polymerization
┌─────────────────────────────────────┐
│        Polyimide (PI) solution       │
└─────────────────────────────────────┘
                │  ← Additive
┌─────────────────────────────────────┐
│          Casting Solution            │
└─────────────────────────────────────┘
                │
┌─────────────────────────────────────┐
│          Filtration (G-3)            │
└─────────────────────────────────────┘
                │  ← Casting
┌─────────────────────────────────────┐
│        Nascent PI membrane           │
└─────────────────────────────────────┘
                │  ←      Solvent
                │         evaporation
   Coagulation →│
┌─────────────────────────────────────┐
│          Wetted Membrane             │
└─────────────────────────────────────┘
                │
┌─────────────────────────────────────┐
│            Evaluation                │
└─────────────────────────────────────┘
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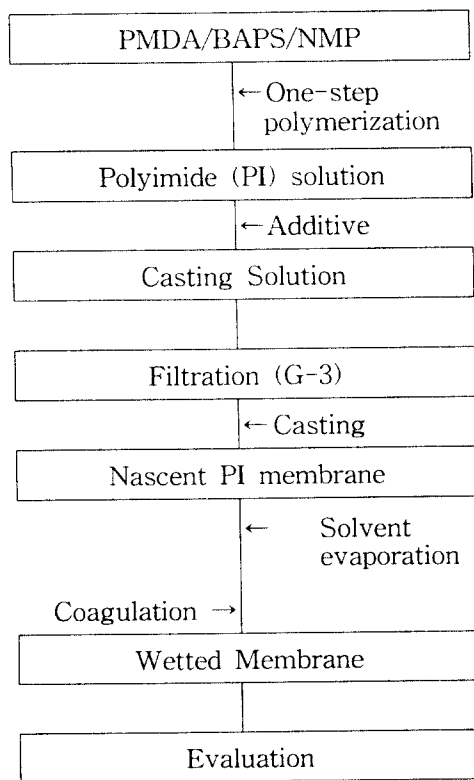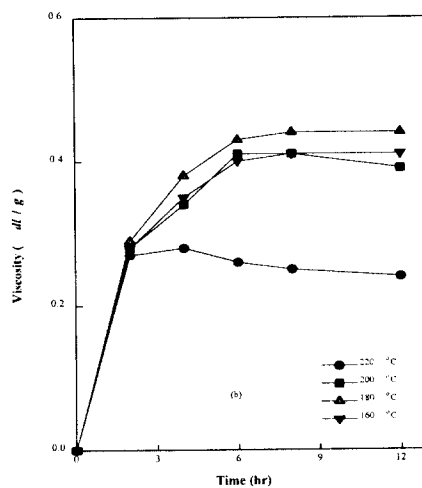
Fig. Experimental procedure.



Fig 2. The viscosity of PI as functions of time and temp.

## Table.1 Solubility of PI prepared from one-step polymerization.[*]

| Solvent | Solubility |
|---|---|
| Acetic acid | × |
| Acetone | × |
| 1-Butanol | × |
| Chlorobenzene | × |
| Diethyl ether | × |
| Ethanol | × |
| Foramide | × |
| Formic acid | × |
| Methanol | × |
| 1-Propanol | × |
| Toluene | × |
| Tetrahydrofuran | × |
| Pyridine | △ |
| DMAc, NMP, DMF etc | ○ |

[*]The PI was immersed in each solvent at 25℃ for 7 days before testing. Where ○ is soluble, △ is swell, and × is insoluble in solvent.
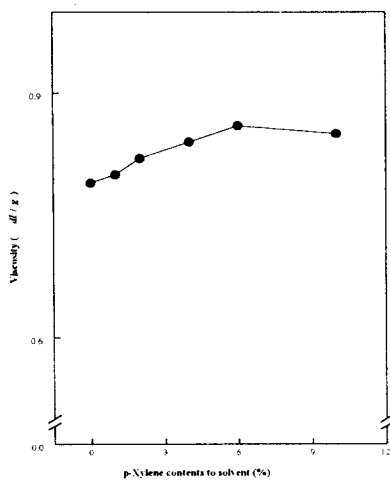


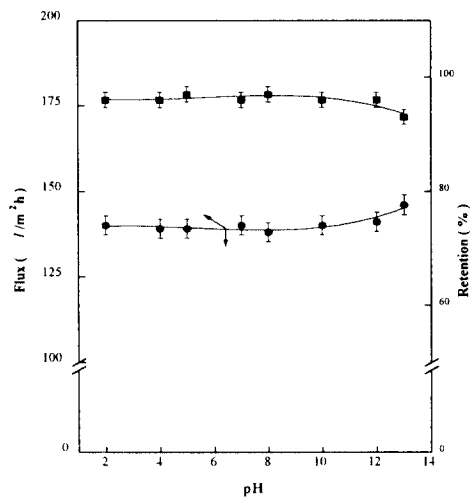Fig 3. Evolution of the viscosity of PI vs amount of azeotroping agent.

Fig. 4. Permeation characterization of the PI membrane as a function of pH.

Table.2 Evaluation of organic Solvent Resistance PI membrane.[a]

| Solvent | PWF ($\ell$/m²hr) | SR[b] (%) |
|---|---|---|
| Acetic acid | 140±5 | 85±5 |
| Acetone | 140±5 | 85±5 |
| Benzene | 140±5 | 85±5 |
| 1-Butanol | 140±5 | 85±5 |
| Chloroform | 140±5 | 85±5 |
| Diethyether | 140±5 | 85±5 |
| Ethanol | 140±5 | 85±5 |
| Foramide | 140±5 | 85±5 |
| Formic acid | 140±5 | 85±5 |
| Methanol | 140±5 | 85±5 |
| 1-Propanol | 140±5 | 85±5 |
| Toluene | 140±5 | 85±5 |
| Pyridine | > 200 | 40±10 |

a)The PI membrane was immersed in each solvent at 25 ℃ for 7 days before testing.
b)Feed solution was 1,000 ppm PEG (MW: 20,000) solution.