Structure-Property Relationships in Aromatic Polyimide:  
2. Optimum Conditions for High Molecular Weight 
Poly(amic acids) and Polyimides

Chung-Ha Jung*, Jung-Min Hwang, Hwan-Jae Choi**, and Soonja Cho†
Institute of Polymer Science and Engineering, Department of Chemical Engineering, Inha University, Incheon 402-751, Korea 
*Hyundai Heavy Industry, Division of Plant Project, Ulsan, 682-792, Korea 
**Kumho & Co., Inc., R & D Center, Kwangju 506-040, Korea 
(Received April 18, 1994)

Abstract: Poly(amic acids) (PAAs) prepared from the mixtures of aromatic dianhydrides [PMDA(pyromellitic dianhydride), ODPA(4,4'-oxydiphthalic anhydride)] and aromatic diamines [3,3'-DDS, 4,4'-diamino diphenyl sulfone, 3,3'-diamino diphenyl sulfone, DDM(4,4'-diamino diphenyl methane)] were thermally cured to convert polyimides (PIs). (1) The optimum condition of polymerization, (2) the effect of monomer purity and the type of PAA(s) (film or powder) on the molecular weight were investigated by measuring the intrinsic and inherent viscosity and molecular weight of the PAAs. The degree of imidization was obtained using FT-IR and the glass transition temperatures were measured using DSC or DMA. Solubilities of the fully imidized PIs were tested in polar and non-polar solvents. Thermal analysis using TGA revealed that thermal stabilities of the PIs depend on their molecular weights and the shape of PAAs as well.

Keywords: aromatic polyimide, structure-property.
INTRODUCTION

Recently a novel class of polymer has successfully prepared to be useful for a wide variety of applications requiring high temperature materials. Above all, polyimides are mainly used in film form, as coatings and composite matrix resins, which are characterized by high thermal stability, electrical resistance and modulus, as well as outstanding chemical resistance. In spite of their wide uses and various patents about the formation of aromatic polyamic acid and polyimide, commercial developments has resulted a little. The papers reported recently are concerned with the preparation and properties of the polyimides consisting other connecting groups between rings, and the effects of these groups upon physical properties and thermal stability.

In this work, we have studied the optimum condition of the polymerization for high molecular weight of PI for film formation, and the relationships between molecular weight and physical and thermal properties using the PAA's and PI's formed from PMDA(pyromellitic dianhydride) and ODA(4,4'-oxydiphthalic anhydride) with various diamines consisting of 3,3'-DDSO₂ (3,3'-diamino diphenyl sulfone), 4,4'-DDSO₂ (4,4'-diamino diphenyl sulfone) and DDM(4,4'-diamino diphenyl methane). These monomers were chosen for commercial purposes in terms of material resources, cost and applicability. In particular, the effect of monomer purity on molecular weight was studied by measuring the inherent and intrinsic viscosity as well as the secondary molecular weight measurement by GPC using THF as a mobile phase.

EXPERIMENTAL

Materials. The aromatic dianhydride and diamine monomers used in this study are shown in Fig. 1. Pyromellitic dianhydride(PMDA: Chriskev Co. Kansas, USA) was purified by sublimation and 4,4'-oxydiphthalic dianhydride(O- DPA: Chriskev Co. Kansas, USA) was recrystallized from methyl ethyl ketone(MEK) before sublimed. 3,3'-diamino diphenyl sulfone(3,3'- DDDO₂) and 4,4'-diamino diphenyl sulfone (4, 4'-DDDO₂) obtained from Chriskev Company, and 4,4'-diamino diphenyl methane (DDM) from Hodagaya Company, Japan, were recrystallized from ethanol.

N,N'-dimethyl acetamide(DMAc; Janssen Co. Belgium) used as a solvent for polymerization was distilled at room temperature with CaH₂ and used for viscosity measurements. N,N'-dimethyl formamide(DMF), N-methyl-2-pyrrolidinone(NMP) and chloroform obtained by commercial sources were directly used as received for solubility test. HPLC grade THF used for GPC mobile phase was obtained from EM Science, Gibbstown, New Jersey, U.S.A.

Preparation of Polyamic acid and Polyimide. Polyamic acid solutions were prepared according to the procedures described in published literatures. Using a three-neck reactor equipped with an overhead stirrer and nitrogen
outlets, diamine solutions were prepared at a constant solid concentration in DMAc. After adding dianhydride powder into diamine solution in a stoichiometric ratio, the solution was slowly stirred at a constant temperature for 5~30 hr.

In order to determine the optimum condition of polymerization for polyamic acid, the effects of monomer purity, various monomer concentration (5~30%) and reaction temperature (5°C, 25°C, and 65°C) were investigated by measuring the viscosity of polymerizing medium at given time intervals.

Two different types of PAA sample were prepared and studied in terms of the effect of viscosity; (1) poly(amic acid)(PAA) film was cast on a glass plate and, DMAc was removed at 70°C for 24 hr. (2) PAA powder was obtained by dropping PAA solution into distilled water as a non-solvent, followed by isolating it for drying at 70°C in a vacuum oven. Later, two sorts of PAAAs were dissolved in DMAc for viscosity measurements.

PAA film or powder was then thermally cured at desired temperature to convert to a PI medium, and then to convert to a corresponding PI at fully imidizing temperature, which is 20°C higher than the \( T_g \) for 2 hours in a vacuum oven.³

Solubility of the prepared PAAAs or PIs were tested at room temperature in such solvents as N,N'-dimethyl acetamide(DMAc), N,N'-dimethyl formamide(DMF), tetrahydrofuran(THF) and chloroform.

**Instrumentation.** Fourier Transform Infra-red(FT-IRs) spectra were recorded with Bruker IFS548 using 16 scans at a resolution of 2 cm\(^{-1}\) for the measurement of polymerization and the degree of imidization.

The glass transition temperature of ODPA based polyimides, which was taken as a midpoint of the transition, was measured on a Perkin-Elmer DSC-7 with a heating rate of 20°C/min under nitrogen atmosphere. Dynamic mechanical analysis was performed on a DuPont DMA 983 at 1 Hz with a heating rate of 3°C/min for the measurement of damping factor tanδ or \( E'' \) of PMDA based polyimides.

A Perkin-Elmer TGA-7 was used to evaluate a weight residue of the PIs up to 900°C and a temperature of 5% weight loss (taken as the decomposition temperature, \( T_d \)) of PIs at a heating rate of 20°C/min under nitrogen purge.

Viscosity of PAA solution(0.5wt%) taken from the reaction(polymerization) bottle in a given time interval was measured to study the reaction time dependence on viscosity by using an Ubbelohde suspended level viscometer. In addition, relative viscosity of a dilute PAA solution prepared by dissolving the PAA film or powder in DMAc was measured to obtain inherent, reduced and intrinsic viscosity at 35°C and averaged in five measurements. The values in each measurement was reproducible within 0.05% error.

For molecular weight and distribution of molecular weight, the PAA powder or film was dissolved in THF and experiments were performed by a Waters 510 GPC with a refractive index detector using THF as a mobile phase at 1 ml/min. Calibration of molecular weights was performed by using monodisperse polystyrene standard sample with ultrastyragel columns connected in series, 500, 10³, 10⁴, 10⁵Å.

**RESULTS AND DISCUSSION**

**The degree of imidization.** In FT-IR spectra studies of polyimides, an internal standard peak is the most important factor as to how sensitive it is to the various changes involved in the curing of polyimides. Ginsberg and Susko⁶ suggested that 1776 cm\(^{-1}\) carbonyl absorbance was fairly well isolated from the rest of the spectrum and resulted in a good reproducibility. Navarre⁷ found that the FT-IR bands at 1780 cm\(^{-1}\)(symmetric carbonyl stretching band) and 720 cm\(^{-1}\)(deformation or carbonyl stretching of
imide ring) were insensitive in high temperature stage of reaction. Pyride\textsuperscript{10} suggested that the absorption near 1500 cm\textsuperscript{-1} attributed to the ring breathing modes of the aromatic moieties appeared to be the most satisfactory as internal standards.

In this study, the technique employed for the degree of imidization was the method of comparing band ratio,\textsuperscript{8,10} i.e., the area of the characteristic bands of imide ring at the 1780 cm\textsuperscript{-1}, 1370 cm\textsuperscript{-1} (C-N stretching), and 720 cm\textsuperscript{-1} was compared with the absorption band at 1720 cm\textsuperscript{-1} or 1480 cm\textsuperscript{-1} which was chosen as internal standards. Thus, the degree of imidization based on 1720 cm\textsuperscript{-1} internal peak for the PMDA/3,3'-DDSO\textsubscript{2} system is compared with the one based on 1480 cm\textsuperscript{-1} peak in Fig. 2 and 3, respectively; as a result, normalized at 720 cm\textsuperscript{-1}/1480 cm\textsuperscript{-1} is rather reliable than the others. The degree of imidization was calculated in this method during the performance of this project and the values at various curing temperature is described in Table 2.

![Fig. 2. Conversion of PI(PMDA/3,3'-DDSO\textsubscript{2}) as a function of curing temperature by using the 1729 cm\textsuperscript{-1} internal standard peak.](image)

![Fig. 3. Conversion of PI(PMDA/3,3'-DDSO\textsubscript{2}) as a function of curing temperature by using the 1480 cm\textsuperscript{-1} internal standard peak.](image)

![Fig. 4. FT-IR spectra of PMDA/DDM in 4000-
4000 cm\textsuperscript{-1} (a) poly(amic acid) (b) fully imidized polyimide.](image)
Optimum Conditions for High Molecular Weight Poly(amic acids) and Polyimides

**Fig. 5.** TGA thermograms of PMDA/3,3'-DDSO₂ in various sample forms (heating rate of 20 °C/min under N₂ gas).

**Fig. 6.** TGA thermograms of various PI powder synthesized from purified monomer (heating rate of 20 °C/min under N₂ gas).

The representative FT-IR spectra between PAA and PI after fully imidized (the condition for fully imidization is curing the PAA at 20 °C higher than its Tₘ for 2 hrs³) are respectively shown in Fig. 4(a) and 4(b) in ODPA/4,4'-DDSO₂ system. In fully imidized PI films, no evidence of DMAc peak was observed at 1650 cm⁻¹.

**Thermal stability.** In Fig. 5, the thermal stabilities of PMDA/3,3'-DDSO₂ produced by purified (Fig. 5(a) and (b) and non-purified (Fig. 5(c)) monomers were compared in terms of sample forms in film or powder. As seen in this figure, the thermal stability of PI synthesized from purified monomer is relatively enhanced. The TGA thermograms of the various PI powders formed from the purified monomers are plotted in Fig. 6. The weight residue between 500 °C and 900 °C was higher in PMDA based system than in ODPA based one, and in all system, a slight weight loss is observed at between 100 °C and 150 °C. The former behavior may arise from the chain stiffness of the PMDA and the latter may result from a volatile such as moisture uptake during experiment. Decomposition temperature, Tₘ, defined as 5% weight loss of the PI in Table 1 shows higher value in PMDA based PIs than in ODPA based PIs, where describes the higher thermal stability in PMDA than in ODPA.

**Glass Transition Temperature (Tₘ).** DSC thermograms of the ODPA based polyimides are drawn in Fig. 7. In this figure, relatively flexible structure (ODPA/3,3'-DDSO₂, in Fig. 7(a)) shows lower Tₘ (246 °C) than the one (262 °C) of rigid structure (ODPA/4,4'-DDSO₂ in Fig. 7(b)). This is the same result as in the previous report,³ of which the meta-substituted moiety has a bigger steric hindrance than the para-substituted one. PMDA/3,3'-DDSO₂, which apparently has a bigger steric hindrance showed its Tₘ at 327 °C (in Fig. 7(d)). However, the rest of the PIs synthesized with PMDA was not traced its Tₘ by DSC. This may be the same case as the PMDA/ODA system of which the Tₘ was not observed on DSC, but was observed at 399 °C on DMA. Thereby, the Tₘ of PMDA/DDM
Table 1. Physical and Thermal Properties of Various PAA/PI Systems

<table>
<thead>
<tr>
<th>System</th>
<th>PAA</th>
<th>PI</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_c (g/mol)$</td>
<td>$M_w/M_c$</td>
<td>IV$^*$</td>
</tr>
<tr>
<td>A</td>
<td>12,900</td>
<td>1.20</td>
<td>0.58</td>
</tr>
<tr>
<td>non-purified</td>
<td>63,000</td>
<td>1.30</td>
<td>0.66</td>
</tr>
<tr>
<td>purified</td>
<td>12,000</td>
<td>1.22</td>
<td>0.56</td>
</tr>
<tr>
<td>B</td>
<td>59,000</td>
<td>1.30</td>
<td>0.60</td>
</tr>
<tr>
<td>C</td>
<td>22,900</td>
<td>1.18</td>
<td>0.67</td>
</tr>
<tr>
<td>non-purified</td>
<td>80,000</td>
<td>1.30</td>
<td>0.82</td>
</tr>
<tr>
<td>purified</td>
<td>2,900</td>
<td>1.21</td>
<td>0.17</td>
</tr>
<tr>
<td>D</td>
<td>12,000</td>
<td>1.13</td>
<td>0.25</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>-</td>
<td>0.18</td>
</tr>
<tr>
<td>non-purified</td>
<td>-</td>
<td>-</td>
<td>0.79</td>
</tr>
<tr>
<td>purified</td>
<td>-</td>
<td>-</td>
<td>1.34</td>
</tr>
</tbody>
</table>

$^a$Intrinsic viscosity $^b$:0.5wt% solution (powder) in DMAC(60/40), 5wt% in DMAC (with fully imidized PI). P.S: Partially soluble, I: Insoluble, *Unknown $T_d$, assumption: 300–400$^\circ$C

Table 2. Solubility of PAA and PI’s Cured at Various Temperature

| System | Curing Temp.(\(^\circ \)C) | DMAC | DMF | THF | CHCl$_3$ | System | Curing Temp.(\(^\circ \)C) | DMAC | DMF | THF | CHCl$_3$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>246$^\circ$C$^*$</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>PAA</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>128$^\circ$C (24%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>128$^\circ$C (27%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>158$^\circ$C (31%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>158$^\circ$C (45%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>198$^\circ$C (42%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>198$^\circ$C (51%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>220$^\circ$C (84%)</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>1</td>
<td>220$^\circ$C (89%)</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>240$^\circ$C (91%)</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>1</td>
<td>260$^\circ$C (97%)</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(II)</td>
<td>271$^\circ$C$^*$</td>
<td>P.S</td>
<td>P.S</td>
<td>1</td>
<td>1</td>
<td>P.A.</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>128$^\circ$C (20%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>178$^\circ$C (21%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>158$^\circ$C (40%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>225$^\circ$C (53%)</td>
<td>SW</td>
<td>SW</td>
<td>SW</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>216$^\circ$C (74%)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>275$^\circ$C (68%)</td>
<td>SW</td>
<td>SW</td>
<td>SW</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>230$^\circ$C (84%)</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>1</td>
<td>313$^\circ$C (87%)</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>260$^\circ$C (93%)</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>1</td>
<td>332$^\circ$C (93%)</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(V)</td>
<td>350$^\circ$C$^*$</td>
<td>P.S</td>
<td>P.S</td>
<td>1</td>
<td>1</td>
<td>Fully imidized PI</td>
<td>P.S</td>
<td>P.S</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>178$^\circ$C (27%)</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>1</td>
<td>178$^\circ$C (24%)</td>
<td>S</td>
<td>S</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>225$^\circ$C (45%)</td>
<td>SW</td>
<td>S</td>
<td>1</td>
<td>1</td>
<td>225$^\circ$C (31%)</td>
<td>S</td>
<td>P.S</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>275$^\circ$C (51%)</td>
<td>SW</td>
<td>SW</td>
<td>1</td>
<td>1</td>
<td>275$^\circ$C (42%)</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>320$^\circ$C (89%)</td>
<td>I</td>
<td>I</td>
<td>1</td>
<td>1</td>
<td>313$^\circ$C (84%)</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>340$^\circ$C (97%)</td>
<td>I</td>
<td>I</td>
<td>1</td>
<td>1</td>
<td>332$^\circ$C (91%)</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ODPA/3.3$'-$DDSO, $^b$ODPA/4.4$'-$DDSO, $^c$ODPA/DDM D; PMDA/3.3$'-$DDSO, $^d$PMDA/4.4$'-$DDSO, $^e$PMDA/DDM

$^*$Intrinsic viscosity; $^1$Degree of imidization by calculation of peak area 720/1480cm$^{-1}$; $^\gamma$-Assumption, $^\gamma$-by DMA

682 Polymer(Korea) Vol. 18, No. 5. September 1994
Fig. 7. DSC thermograms of polyimides powder (heating rate of 20°C/min under N₂ gas).
(a) ODPA/3,3'-DDS0₂ (b) ODPA/4,4'-DDS0₂ (c) ODPA/DDM (d) PMDA/3,3'-DDS0₂ (e) PMDA/4,4'-DDS0₂ (a) PMDA/DDM

Fig. 8. DMA thermogram of PMDA/DDM polyimides (heating rate of 3°C/min in air).

measured by DMA was shown at 345°C by £ (in Fig. 8) with small amplitude of the peak. For the entire system except PMDA/3,3'-DDS0₂, the film formation from purified monomer was available with 15wt.% solution. We believe that the technique for film formation is needed for further development.

Solubility. The solubility of PAAs and PIs cured at various temperature was investigated and the results are listed in Table 2. ODPA based PIs show better solubility than PMDA based PIs. In addition, fully imidized PIs based

ODPA are partially soluble in DMAc or DMF which is a polar solvent. Solubilities of the PIs are correlated with the chemical structure, thermal stability and the glass transition temperature. Thus, the more flexible structure, the lower thermal stability and Tg, and the higher solubility are observed.

Viscosity. The reaction concentration and reaction temperature dependency on the inherent viscosity of PAAs in PMDA/3,3'-DDS0₂ and ODPA/3,3'-DDS0₂ formed from purified monomers were measured and plotted as a function of reaction time in Fig. 9(a) and Fig. 9(b). ODPA system showed higher viscosity than PMDA system. 15 wt% solution shows higher viscosity than the one measured at 5wt% or 30wt% in concentration. In addition, the inherent viscosity, measured at 25°C was relatively
higher than that at 5°C or at 65°C. Thus, the maximum condition for high molecular weight was a reaction of 15 wt% in concentration at 25 °C for at least 5 hours. In comparison, inherent viscosity of the ODPA system (A, B, and C in Table 1) shows approximately four times higher than that of PMDA system (D and F in Table 1). Molecular weight of the ODPA system is as well. In addition, electron affinity of PMDA and ODPA is 1.9 eV and 1.3 eV, respectively. The difference in electron affinity may induce a formation of high molecular weight PAA such as in ODPA system than PMDA system. We will come to this again in the later section.

Dilute PAA solution for the measurement of inherent and reduced viscosity was prepared from the once precipitated powder or film. The intrinsic viscosity of the above PAA is obtained by extrapolation at zero concentration from the inherent viscosity. In Fig. 10, the inherent and reduced viscosity of the purified PMDA/4,4'-DDSO 2 system was increased with lower concentration and as a result, the intrinsic viscosity at the zero concentration is 0.22dℓ/g for film (Fig.10-(a)) and 0.18dℓ/g (Fig. 10-(b)) for powder. The difference in intrinsic viscosity may arise from the original sample form (film or powder) or polyelectrolyte effect of DMAc. As will be discussed later, extrapolation of the inherent viscosity at zero concentration was performed without considering the polyelectrolyte effect which was significantly observed in this experiment (arrows in Fig. 10). As in Fig. 10-(a) and (b), the upturn behavior in viscosity at low concentration is what we believe to be arrived from the polyelectrolyte effect of the polar solvent, DMAc. Thus we suggest that the exact intrinsic viscosity may vary. The values of inherent and reduced viscosities were also used to calculate [η] in Huggins and Kraemer equation. In contrast, the calculated inherent and reduced viscosities of the PMDA/4,4'-DDSO 2 system synthesized by non-purified monomers were 0.09dℓ/g in film form and 0.07dℓ/g in powder, which are concurrently decreased with lower concentration and extremely low value. Precipitating PAA solution in water is reported to give rise to a reduced molar mass. This behavior also induces that the intrinsic viscosity of non-purified system is lower than that in purified system and that the molecular weight of PMDA system is relatively lower than ODPA system. This is the similar result as Wallach 11 reported.

**Average molecular weight.** The number average molecular weight (Mn) and polydispersity (Mn/Mw) by GPC are listed in Table 1 for the system studied. It has not been often to report the molecular weight of polyimide because of poor solubility. We have approached to measure molecular weight of PAA powder dissolved in THF using GPC with a mobile phase, THF. For the purified ODPA system, the observed number average molecular weight is 59,000–80,000. This is fairly reasonable data compared to the non-purified ODPA system in which (Mn) is 13,000–23,000. The latter is relatively four times lower than the purified one.
and this correlates to the viscosity difference in two different systems.

PMDA/3,3'-DDS\textsubscript{3} system shows extremely low value of molecular weight and the trend is similar to the intrinsic viscosity. Molecular weight of the PMDA/4,4'-DDS\textsubscript{3} and PMDA/DDM systems was not available due to poor solubility in THF. From the above observation, we believe that molecular weight of PAAs using THF is not influenced by the polyelectrolyte effect of the solvent. However, DMAc or DMF as a mobile phase is believed to give a severe polyelectrolyte effect by polarity or impurity (amine group). Polyelectrolyte effect of polar solvent on molar mass is under investigation and will be disclosed shortly.

CONCLUSIONS

Using the purified and non-purified monomers (dianhydride and diamine), the polyamic acid and polyimide were synthesized and they are dependent on the purity of monomer, reac
tion temperature, and monomer-solvent concen
tration. In this reaction, the reactivity of elec
trophilic dianhydride may be correlated with its electron affinity, while the reactivity of nu
cleophilic diamine may be correlate with its basic
ity. The structural changes in diamine affect the reaction rate more than changes in dianhy
dride. Optimum conditions for high molecular weight PAAs measured by the viscosity and GPC technique are resulted in a reaction with purified monomer at 25°C, with 15wt% concentra
tion for 5 hours. Less flexible PI moiety shows high $T_g$ and an enhancement in thermal property. Molecular weight of PI was also influ
cenced by monomer purity as well as the poly
electrolyte effect induced by impurity of sol

vent.

Acknowledgment. This work was supported by the Ministry of Education Research Fund for Advanced Materials in 1991 – 1992, and partially supported by the Dong-Sung Chemical Industry Co., Ltd. S. Choe is particularly grateful to the president, Jung-Ho Paek and the former vice-president, Byung-Kwon Choi, of the Dong-Sung Chemical Ind. Co., Ltd., for their continual support in performing research and in purchasing GPC instrument.

REFERENCES

2. H. J. Jeong, Y. Oishi, M. Kakimoto, and Y. Imai, 
3. S. K. Kim, C. H. Jung, H. S. Kim, and S. Choe, 
Polymer (Korea), 6, 249 (1992).
4. G. Kolesnikov, O. Fedotova, E. Hofbauer, and 
V. Shelegayaeva, Visokomol. Soedin., A9, 612 
(1967).
7. A. K. St. Clair, T. L. St. Clair, W. S. Slep, and 
K. S. Ezrell, NASA TM-87650. NASA, Washing
thesis and Characterization”, Ed. by K. L. Mittal, 
acterization”, Ed. by K. L. Mittal, vol. 1, pp. 259 
(1967).