

工業用플라스틱에 關한 研究( I )  
— 全芳香族 폴리아미드의 縮重合에 있어서  
分子量에 影響을 미치는 因子에 關하여

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(1982년 8월 16일 접수)

**A Study on the Engineering Plastics( I )**  
**— Factors Affecting the Molecular Weight in the**  
**Polycondensation of Wholly Aromatic Polyamides**

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(Received August 16, 1982)

요약 : 高强度 · 高彈性率을 갖는 全芳香族 polyamide를 低溫縮重合法으로 重合하고 高重合度의 高分子을 合成하기 위한 主要因子를 考察하였다. 界面縮重合의 경우, acid chloride를 약 5% 過量으로 사용할 때 高分子量의 poly(m-phenyleneisophthalamide) [MPD-I]가 얻어졌으나 poly(p-phenyleneterephthalamide) [PPD-T]의 重合은 어려웠다. 溶液縮重合의 경우에는, 極性 amide類의 溶媒에서 比較의 高重合度의 全芳香族 polyamide가 얻어졌으며 PPD-T의 重合에 있어서는 單量體의 濃도가 7wt%일 때가 가장 좋았으며 酸捕捉劑로서는 pyridine이 triethylamine보다 더 效果的이었다.

**ABSTRACT :** Wholly aromatic polyamides were synthesized by the low temperature polycondensation and the factors which affect the polycondensation were studied. A relatively high molecular weight poly(m-phenyleneisophthalamide) [MPD-I] was obtained by the interfacial polycondensation when 5 mole % excess of isophthaloyl dichloride was used, but it was very difficult to obtain a high molecular weight poly(p-phenyleneterephthalamide) [PPD-T]. In case of the solution polycondensation, relatively high molecular weight wholly aromatic polyamides [PPD-T and MPD-I] could be obtained by the use of a polar amide solvent. In the solution polycondensation of PPD-T, the optimum monomer concentration was about 7 wt % and, as an acid acceptor, pyridine was more effective than triethylamine.

## I. INTRODUCTION

Until recently, ultra-high modulus/strength materials have been obtained by the use of inorganic materials such as E-glass, carbon, asbestos and so on.

However, many recent studies have suggested that the thermally stable and extremely high modulus/strength organic polymers can be synthesized by incorporating stable aromatic rings into the polymer chain.

Since the earliest patent<sup>1</sup> for ultra-high modulus/strength polymer was reported in 1961, a lot of studies on these type polymers<sup>2</sup>, eg, aromatic polyamide, aromatic polyester, aromatic polyazo, aromatic polyazomethine etc, have been made.

The physical properties of some ultra-high modulus/strength polymers are listed in Table I.

As shown in Table I, for their superior properties the demand for special purposes, e.g. substitute for metal, tire cord and composites for military and aerospace uses etc, is on the increase by leaps and bounds nowadays.

Numerous methods for the syntheses of wholly ordered aromatic polyamides have been reported in patents and papers, but no details to obtain a high molecular weight polymer are well known. So in this study, factors affecting the molecular weight of the polymer during the low

temperature polymerization were examined and discussed.

## II. EXPERIMENTAL

### 1. Purification of the reagents

All the solvents and acid acceptors were dehydrated with powerful drying agents such as calcium hydride and barium oxide and then distilled under the reduced pressure. The purified reagents were stored in a dry box until they were used.

### 2. Preparation of the acid chlorides

#### 2-1. Terephthaloyl dichloride

A 500ml four necked flask equipped with a condenser, a thermometer, a stirrer and a dropping funnel was charged with 100g of terephthalic acid, 2ml of pyridine and 200g of thionyl chloride.

The temperature was raised to 70°C and an additional 200ml of thionyl chloride was added through the dropping funnel for 10hours with stirring. The reaction was continued until the emission of sulfur dioxide and hydrogen chloride ceased and then the excess thionyl chloride was distilled out.

Terephthaloyl dichloride was obtained by distillation at 141°C under 16mmHg. (yield=53.7%, m.p.=81°C)

#### 2-2. Isophthaloyl dichloride

By the analogous method described in II-2-1, isophthaloyl dichloride was prepared from isophthalic acid and thionyl chloride. (yield=57.5% m.p.=43.5°C)

#### 2-3. o-Phthaloyl dichloride

A 500ml three necked flask equipped with a

Table I. Physical properties of U-H M/S polymers

Polymer	Initial modulus (g/den)	Tenacity (g/den)	Elongation to break (%)	Density (g/cm <sup>3</sup> )
X-500T	458	12.1	11.9	1.44
X-500G	718	18.4	3.7	1.47
Kevlar	498	24.8	4.0	1.44
Kevlar-49	1,014	29.8	3.0	1.45
*Steel	215-283	3.7	2.0	7.85

condenser, a thermometer and a stirrer was charged with 100g of phthalic anhydride and 141g of phosphorus pentachloride.

The mixture was refluxed at 150°C for 10 hours with stirring and then the temperature was gradually raised to 250°C to distil off most of phosphoryl chloride by use of a downward condenser.

o-phthaloyl dichloride was obtained by distillation at 132°C under 16mmHg. (yield=45.7%, m.p.=10.5°C)

### 3. Polymerization

#### 3-1. Interfacial polycondensation<sup>3</sup>

Diamine(0.018 to 0.022moles) and sodium hydroxide(0.05moles) were dissolved in water(130 ml) and acid chloride(0.02moles) was dissolved in cyclohexanone(65ml). Both of the solutions were cooled to 3°C, and then the acid chloride solution was added with vigorous stirring into the diamine solution under nitrogen bleeding.

Since the reaction was exothermic, the temperature was controlled below 10°C in a ice and water bath during the reaction.

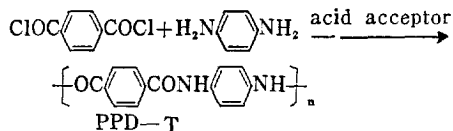
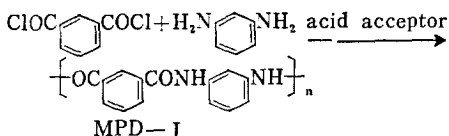
#### 3-2. Solution polycondensation<sup>4</sup>

Diamine(0.02moles) and an acid acceptor(0.01 to 0.03moles) were dissolved in a pure dry solvent (50 to 150ml) and the solution was cooled to 10°C.

Into this solution, the finely powdered acid chloride was poured at once with vigorous stirring under nitrogen bleeding.

During the reaction, the temperature increased above the room temperature.

The reaction schemes are as follows



### 4. Measurement of inherent viscosity ( $\eta_{inh}$ ) of the polymer

Fifty mg. of the polymer was completely dissolved in 10ml of 96% sulfuric acid.

Relative viscosity was measured at  $30 \pm 1^\circ\text{C}$  with the Ostwald viscometer and inherent viscosity was calculated from the equation :

$$\eta_{inh} = \ln \frac{\eta_{rel}}{C}$$

where,  $\eta_{inh}$  : inherent viscosity of the polymer.

$\eta_{rel}$  : relative viscosity of the polymer.

C : concentration of the solution.

## III. RESULTS AND DISCUSSION

### 1. Identification of the polymer

#### 1-1. Infrared spectrum of the polymer<sup>5</sup>

In order to identify the structure of the polymer, the infrared spectrum was taken and shown in Fig.1.

In Fig.1, the three strong bands at  $1660\text{cm}^{-1}$ ,  $1520\text{cm}^{-1}$  and  $1340\text{cm}^{-1}$  represent amide I, amide II and amide III bands of secondary amides, and band at  $3300\text{cm}^{-1}$  indicates  $\nu\text{NH}$  and bands at  $1430\text{cm}^{-1}$  and  $1140\text{cm}^{-1}$  indicate phenyl groups.

In the infrared spectrum of PPD-T, absorption at  $820\text{cm}^{-1}$  suggests p-substituted phenyl groups and in the infrared spectrum of MPD-I, absorptions at  $780\text{cm}^{-1}$  and  $675\text{cm}^{-1}$  suggest m-substituted phenyl groups.

#### 1-2. Elemental analysis of the polymer

To know the polymer composition, elemental analysis was performed with C.H.N. Corder MT-

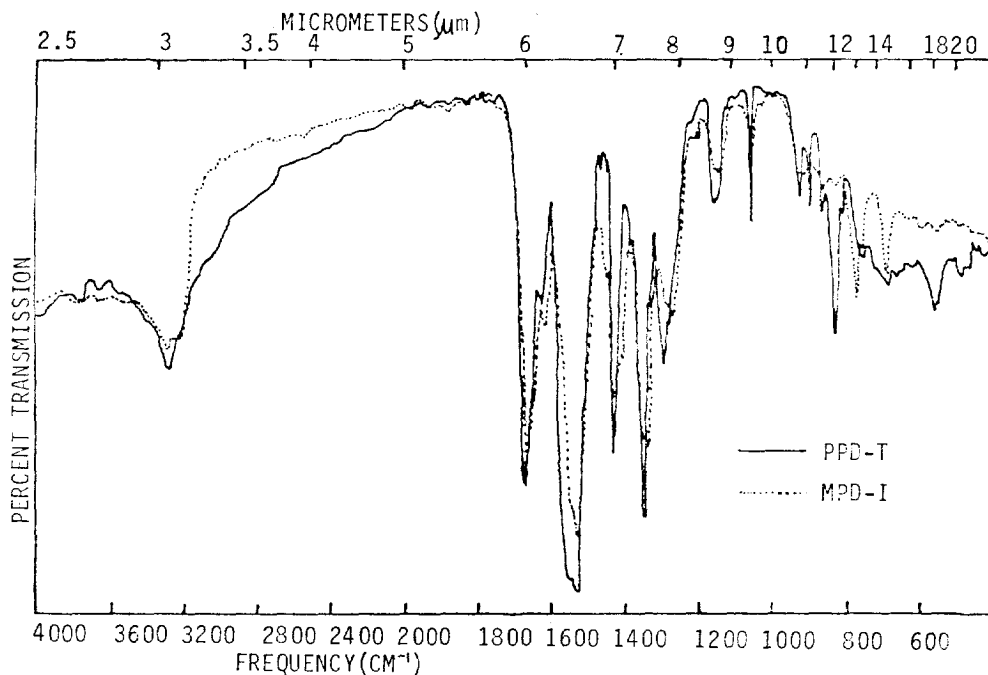


Figure 1. I.R. Spectra of PPD-T and MPD-I.

Table II. Composition of the polymer

	PPD-T		MPD-I	
	calculated	experimental	calculated	experimental
carbon(%)	70.06	65.65	70.06	67.54
hydrogeu(%)	4.18	4.84	4.18	4.27
nitrogen(%)	11.76	11.44	11.76	11.69

2(Yanaco), and the results are listed in Table-II.

## 2. Factors affecting the molecular weight of the polymer

### 2-1. Interfacial polycondensation<sup>3</sup>

A relatively high molecular weight MPD-I was obtained, and it was found that the molar ratio of diamine to acid chloride had a significant influence on the molecular weight of the polymer (Fig. 2).

A little excess use of acid chloride (5%) gave

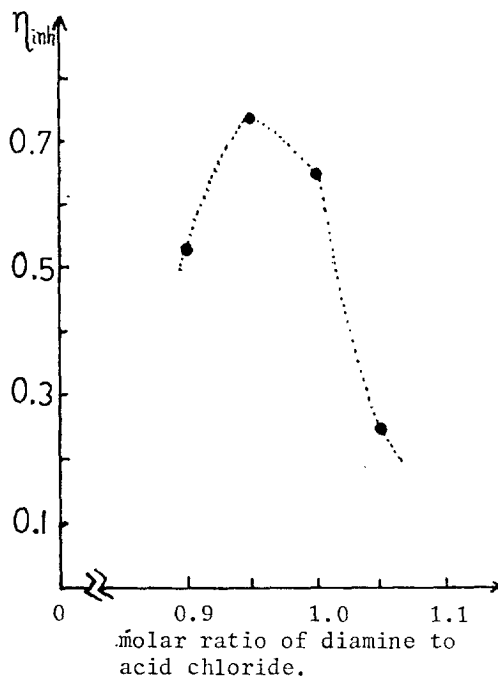


Figure 2. Relation between  $\eta_{inh}$  of MPD-I and molar ratio of diamine to acid chloride.

the better results, which may be due to the partial hydrolysis of acid chloride during polymerization.

It was very difficult to obtain a high molecular weight PPD-T, because there was little chance of growing the polymer chains. In other words, the growing polymer chains were easily precipitated due to the insolubility and the strong intermolecular attraction at the early stage of polymerization.

### 2-2. Solution polycondensation<sup>4</sup>

In solution polycondensation, a high molecular weight MPD-I ( $\eta_{inh} \geq 0.72$ ) could be easily obtained but the polymerization of PPD-T required optimization of many factors to obtain a high molecular weight polymer.

The influence of solvents on the inherent viscosity of PPD-T was shown in Fig. 3, and the conditions of each experiments were listed in Table III.

As shown in Fig. 3, good results were obtained in the mixed solvents of HMPA-NMP(3 : 1, molar ratio) and in the salt added solvents. This suggests that an enhanced results can be obtained by use of a solvent which is polar and has a strong solubilizing power for the growing polymer chains. That is to say, the mixed sol-

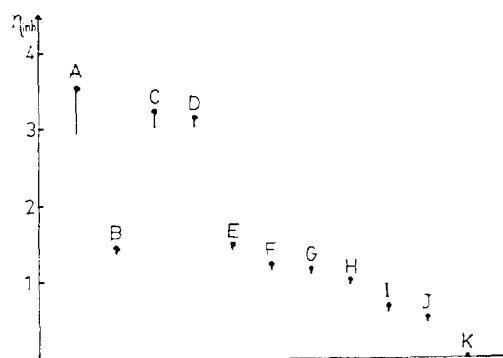


Figure 3. Influence of the solvent on  $\eta_{inh}$  of PPD-T.

vents can easily form a polar complex which can make the growing polymer chains more soluble by polar solvation during polymerization.

Analogously, in the salt added solvents such as NMP-LiCl and DMA-LiCl, the polymer is expected to be solvated by interaction with polar solvent which is formed by the salt-solvent complex<sup>6</sup>. The optimum amount of lithium chloride was about 3 to 3.5wt% (Fig. 4).

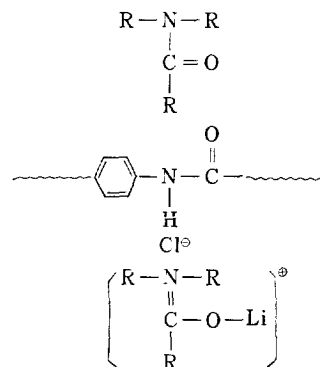


Table III. Conditions of Solution polycondensation

	Solvent	acid acceptor
A	HMPA-NMP	Pyridine
B	HMPA-NMP	Et <sub>3</sub> N
C	NMP-LiCl	Pyridine
D	DMA-LiCl	Pyridine
E	NMP	Pyridine
F	CF-Et <sub>3</sub> N·HCl	Et <sub>3</sub> N
G	DMA	Pyridine
H	DM-Et <sub>3</sub> N·HCl	Et <sub>3</sub> N
I	CF	Pyridine
J	DM	Pyridine
K	DMF	Pyridine

HMPA : hexamethylphosphoramide

NMP : N-methyl pyrrolidone

DMA : dimethylacetamide

CF : chloroform

DM : dichloromethane

DMF : dimethyl formamide

LiCl : lithium chloride

Et<sub>3</sub>N : triethyl amine

Et<sub>3</sub>N·HCl : triethylamine hydrochloride

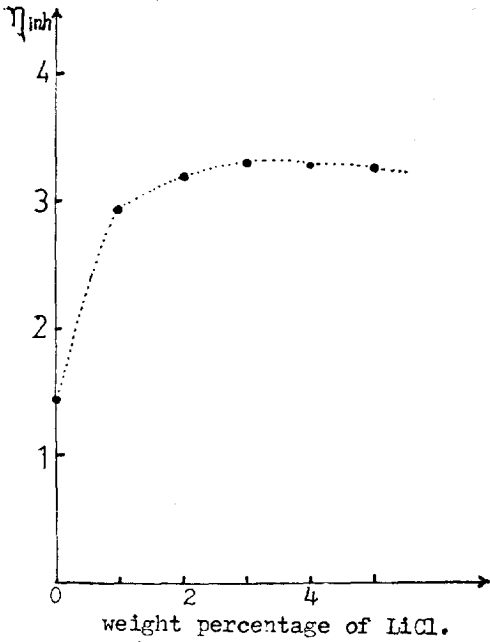


Figure 4. Relation between  $\eta_{inh}$  of PPD-T and amount of lithium chloride.

Due to the low activation energy(1.8kcal/mol) for the reaction between DMF and acid chloride, a high molecular weight PPD-T could not be synthesized in DMF<sup>7</sup>.

Though triethylamine is the more powerful hydrogen chloride acceptor than pyridine, pyridine gave the better results than triethylamine. This is derived from the fact that triethylamine reduces the solubility of diamine in solution(Fig. 5).

The optimum molar ratio of diamine to acid chloride was unity and the optimum monomer concentration was about 6 to 7wt% as shown in Fig. 6 and Fig. 7.

This suggests that in solution polycondensation the hydrolysis of acid chloride is negligible and the growing polymer chain retains its mobility during polymerization due to the enhanced solubility. In fact, at the end of polymerization,

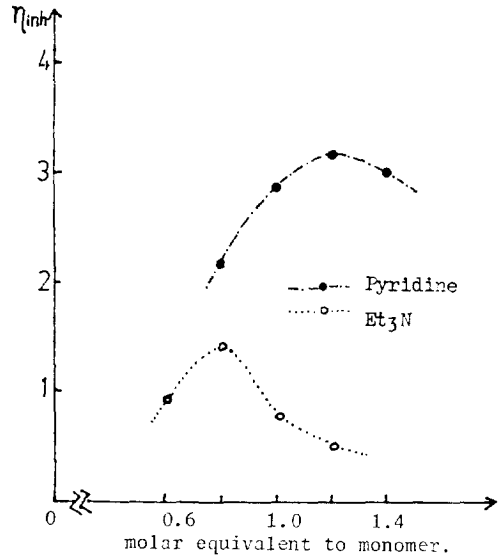


Figure 5. Relation between  $\eta_{inh}$  of PPD-T and the amount of acid acceptor(DMA-LiCl)

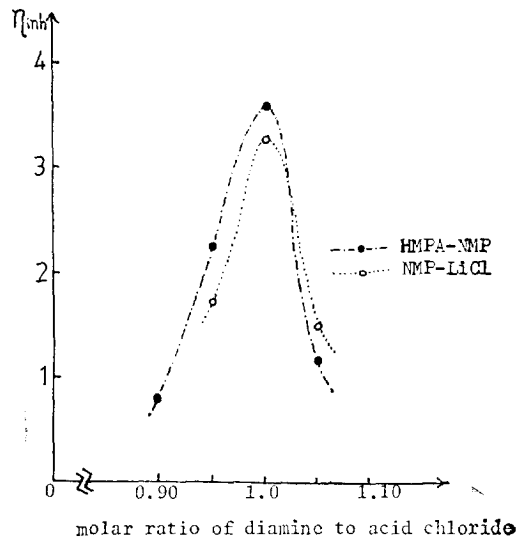


Figure 6. Relation between  $\eta_{inh}$  of PPD-T and molar ratio of diamine to acid chloride

the reaction mixture becomes a yellow gel state or a yellow viscous solution state. Though the post-polymerization took place in both cases, the increase of the inherent viscosity of the polymer by the post-polymerization was larger in the mixed solvents than in the salt added solvent as shown in Fig. 8.

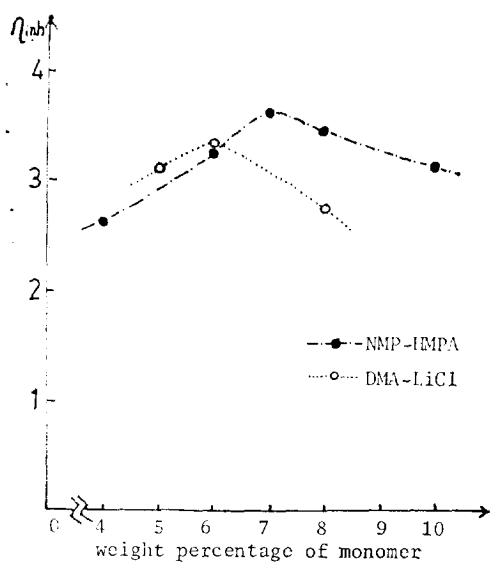


Figure 7. Relation between  $\eta_{inh}$  of PPD-T and monomer concentration.

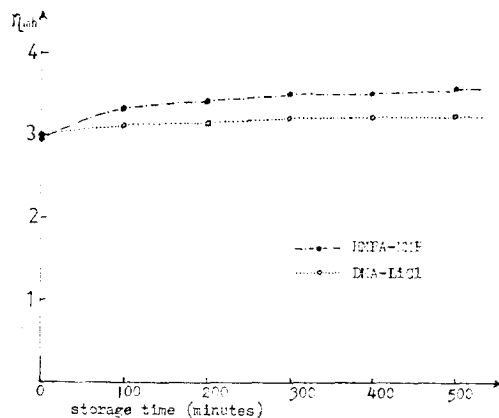
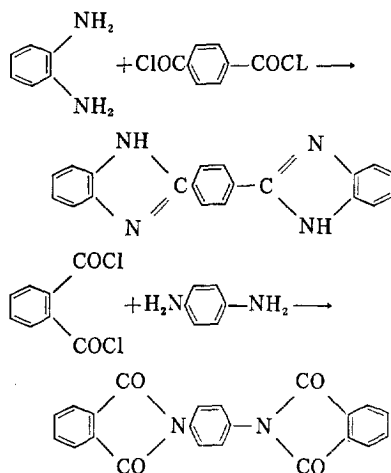


Figure 8. Relation between  $\eta_{inh}$  of PPD-T and storage time.

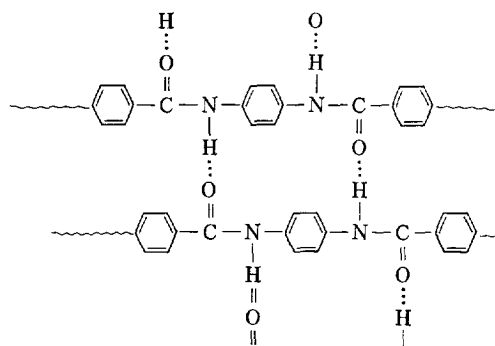
### 2-3. Theoretical considerations

In most cases, incorporation of ortho-monomer resulted in the oligomer formation.

This may be attributed to the side reactions such as imine and imide formation.



In case of PPD-T, the difficulty to obtain a high molecular weight polymer may be ascribed to the poor solubility of the growing polymer chains during polymerization. That is to say, due to the double bond character of amide bond (semi-conjugated linkage) and the rigidity of phenylene ring, PPD-T has an extended(rodlike) conformation in solution. As a result, the intermolecular hydrogen bonding by polar amide



(The dotted line represents the intermolecular hydrogen bonding)

I.V.	$M_w$	$M_w/M_n$
1.84	10,400	1.51
2.30	13,500	1.84
3.06	22,800	2.31
5.12	35,000	3.00

Table IV. Relation between I.V. and molecular weight of PPD-T.

groups becomes more facile, and hence the growing polymer chains easily bundle up together and lose their mobilities at the early stage of polymerization. Therefore, only a low molecular weight polymer can be obtained unless a strong polar solvent is used.

For PPD-T, the relation between inherent viscosity and molecular weight<sup>8</sup> is listed in Table IV.

#### IV. CONCLUSION

1. In case of interfacial polycondensation, a high molecular weight PPD-T could be hardly obtained, but a relatively high molecular weight MPD-I was obtained in which case, the optimum monomer concentration and molar ratio of diamine to acid chloride were 2 to 3wt% and 0.95 respectively.
2. In case of solution polycondensation, a high molecular weight MPD-I was easily obtained and a relatively high molecular weight PPD-T was obtained as well.
  - 1) The optimum monomer concentration and molar ratio of diamine to acid chloride were 6 to 7wt% and 1 respectively.
  - 2) As an acid acceptor, pyridine gave the better result than triethylamine.
  - 3) A relatively high molecular weight PPD-T was obtained in strong polar solvents such as the mixed solvents of HMPA-NMP and the salt-added solvents.

#### REFERENCES

1. Du Pont de Nemours & Co., E.I., B.P. 879, 491.
2. ① *J. Macromol. Sci.-Chem.*, A7(1), 3-348 (1973).  
 ② A. Ciferri and I.M. Ward, "Ultra-high modulus polymers", Applied Science Publishers, London, 1977.  
 ③ 芳香族 ポリアミド系 高弾性率 繊維について 東レ(株)纖維研究所, 津田 禎三, 1975.  
 ④ Monsanto Co. U.S.P. 3,225,011.  
 ⑤ 日本特開昭 47-39,458, 47-43,419.  
 ⑥ U.S.P. 3,575,933.
3. ① P.W. Morgan, "Condensation Polymers: By Interfacial and Solution Methods", Interscience, New York, 1965.  
 ② P.W. Morgan, *J. Polym. Sci.*, Part C, No. 4, 1075(1953).
4. ① P.W. Morgan, *Macromolecules*, 10(6), 1381(1977).  
 ② Mera Hiroshi, Japan Kokai. Tokkyo Koho, 77-71,593(1977).  
 ③ Mera Hiroshi, Japan Kokai. Tokkyo Koho, 78-294(1978).
5. Koji Nakanishi and Philippa H. Solomon, "Infrared Absorption spectroscopy" (2/e), Holdenday, Inc. 1977.
6. M. Panar, *Macromolecules*, 10(6), 1401 (1977).
7. J.A. Fitzgerald, U.S.P. 3,850,888(1974).
8. M. Arpin, *Polymer*, 18, 591(1977).

#### ACKNOWLEDGEMENT

This study has been carried out by aid of the Korea Science and Engineering Foundation(KOSEF). The authors wishes to express their thanks to KOSEF for their financial support throughout this study.