공학석사 학위논문

# Synthesis and Characterization of Novel Wholly Aromatic Poly(ester-amide)s Exhibiting Lyotropic Behavior in Organic Solvent

유기용매에서 유방성 거동을 보이는

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2014년 8월

서울대학교 대학원

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# Synthesis and Characterization of Novel Wholly Aromatic Poly(ester-amide)s Exhibiting Lyotropic Behavior in Organic Solvent

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이 논문을 공학석사 학위논문으로 제출함
2014년 6월

서울대학교 대학원
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2014년 6월

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## Abstract

# Synthesis and Characterization of Novel Wholly Aromatic Poly(ester-amide) Exhibiting Lyotropic Behavior in Organic Solvent

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Aromatic polyamides(aramids) are considered to be high performance materials due to their superior thermal and mechanical properties. But, their poor solubility in organic solvents resulting from the strong hydrogen bonding give to processing difficulties and limit their application. In this study, we synthesized novel wholly aromatic poly(ester-amide)s. To reduce the hydrogen bonding, ester group was introduced. Because the ester group maintained its planarity, it was expected that the chain conformation of polymer was not interrupted, which make the aramids exhibit liquid crystalline behavior with enhanced solubility in organic solvents. By copolymerizing 2 aromatic diamines, the optically anisotropic polymer dopes could be prepared in NMP+$CaCl_2$ system. The dope showed the highest viscosity at 7wt% and the viscosity decreased from 8wt%. The lowest viscosity was observed at 11wt%. From POM images, the formation of liquid crystal started at 8wt%. Thus, these aramids exhibited lyotropic behavior in organic solvent.

**Keywords: Aramids, Liquid crystal, Lyotropic, Aromatic Polyamides, Solubility, Organic solvent, Hydrogen bonding**

**Student Number: 2012-23930**

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# Chapter 1. Introduction

Wholly aromatic polyamides (aramids) are synthetic polyamides in which at least 85% of amide groups are bound directly to 2 aromatic rings. The earliest, simplest, and best known aramids are poly(*p*-phenyleneterephthalamide) (PPTA), poly(*m*-phenyleneisophthalamide) (PMIA) commercialized by Du Pont. These polymers are considered to be high performance materials due to their excellent thermal and mechanical properties.[1,2] Thus, these polymers can be transformed into flame, cut-resistant and high-tensile strength synthetic fibers, with technological applications in the field of coatings and fillers in the aerospace and armaments industry, in asbestos substitutes, electrical insulation, bullet-proof body armor, industrial filters, and sport fabrics, among others. [1,2]

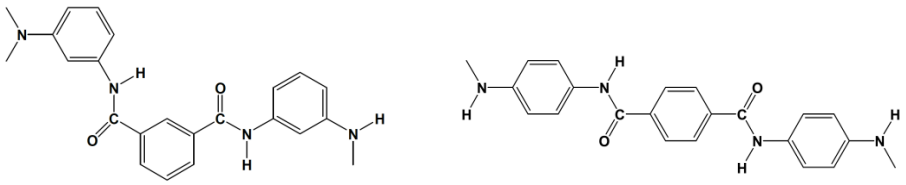


**Fig 1.1** Chemical structure of PMIA (left) and PPTA (right)

However, the application of these aramids is often hampered by problems in their fabrication. First, they are insoluble in common organic solvent. They are only soluble in concentrated sulfuric acid because of their high cohesive energy density resulting from hydrogen bonding (H-bond) of amide groups between the polymer backbone. This high concentration of hydrogen bonding is largely due to the fact that these stiff linear polyamides prefer to align

themselves in parallel arrays, miximizing the accessibility of amide groups to inter-chain H-bond formation, and that the amide groups are spaced along the chains at about even distances, such that the formation of all possible additional H-bonds between the two interacting chains. So, hydrogen bonding between the polymer backbones can be decoupled by concentrated sulfuric acid only. Second, their extremely high transition temperatures lie above their decomposition temperatures due to their high crystallinity and high stiffness of the polymer backbone. Therefore, these aramids cannot be processed by melt spinning or solution spinning in common organic solvents except for concentrated sulfuric acid.

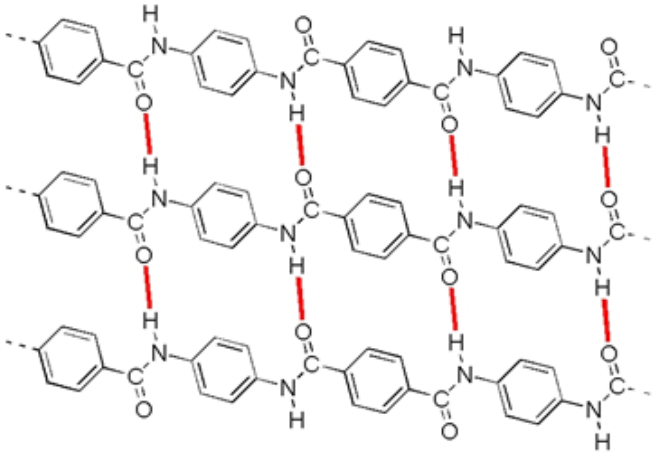


**Fig 1.2** Trans and extended conformation and hydrogen bonding through the polymer backbone of PPTA

As a consequence, basic and applied research is being conducted to enhance their processability and solubility, in order to broaden the scope of their applications. There are several principal ways to increase the solubility of *p*-oriented aromatic polyamides[3,4,5].The first of these is random

copolymerization with minimum amounts of either meta or ortho benzene rings. In order to achieve solubility in organic solvents for PPTA, this approach has been used by copolymerizing either isophthaloyl chloride or *m*-phenylene diamine[4]. These studies concluded that the desired degree of solubility cannot be gained while maintaining average properties of the PPTA chain. Above 5% random incorporation of meta structure, the polymer loses its extended chain conformation.

The second way to increase solubility of aromatic polyamides is to replace an amide hydrogen by an alkyl or aryl group which results in a reduction in hydrogen bonding effect.[6,7] This is a very effective technique for increasing solubility of aromatic polyamides in organic solvents and it has been investigated for PPTA polymers. However, it has been found that even small percentages of *N*-methylation are sufficient to change the hydrodynamic properties of *p*-linked aromatic polyamides. Thus, the Kuhn length of *N*-methylated PPTA is only $1/20^{th}$ of that of the non-*N*-methylated PPTA. It was concluded that *N*-methylation tends to reduce the fraction of amide bonds having a planar trans conformation.

A third means to increase solubility of aromatic polyamides is to employ symmetrical and unsymmetrical substitution on benzene rings. Both symmetrical and unsymmetrical substituents have been studied on the PPTA backbone. The concept of unsymmetrical substitution on benzene rings to increase solubility of aromatic polyamides is more promising because one can have control of chain rigidity, flexibility, solubility and hydrogen bonding with the use of the proper substituent.[8,9]

On the other hand, a unique behavior is derived from highly oriented polymer chain with strong inter-chain H bond of PPTA.[10-13]

It is that PPTA forms liquid crystalline state at a certain concentration. The liquid crystal is a material, which has properties in between liquid and solid state with respect to crystal structure.. Liquid state has short-range order and long-range disorder, whereas solid has short and long-range order. When the molecular arrangement is in between the 2 states, then it is called liquid crystal. Sometimes, it is called mesophases, mesomorphic phases, or anisotropic fluids. Because the liquid crystalline state is optically anisotropic, the liquid crystalline solution is opaque liquid. Heat or solvent may bring liquid crystal formation. When solvent produces liquid crystal, it is called lyotropic and if temperature, thermotropic.

PPTA is the lyotropic material. It is well understood that the behavior of rigid and flexible molecules is different. Flexible molecules such as nylon in dilute solution have low levels of entanglement. But in concentrated solution the random coils become highly entangled so that spinning and drawing leads to only partially extended chains. But, the behavior of rigid rod-like molecules in solution are different from a conventional flexible polymers. Rigid molecules like *p*-aramids cannot form random coils when their solutions are concentrated, because their movement is restricted. So at a critical concentration, they cannot populate the solution randomly. Under such a condition, for packing more molecules within the solvent, they are forced to align parallel to each other and the liquid crystalline state is formed. The liquid crystalline states can be recognized by visual observation, turbidity,

opalescence upon stirring, polarized optical microscopy, solution viscosity and orientation in magnetic field.

Generally the more the concentration of polymer solution increase, the more viscosity of polymer solution increase. But, in this case when the liquid crystalline domain is formed, a slippage of the liquid crystalline domain of rigid rod-like chain become easier. As a result, although the concentration of solution increase, the viscosity of PPTA solution start to decrease and the solution can flow more easily to the direction of the applied shear force. So, in case of spinning of PPTA polymer this characteristic is used. Due to the shear force in spinneret capillary, the liquid crystalline phase orients in the direction of deformation leading to fully extended chains of fibers with high strength.

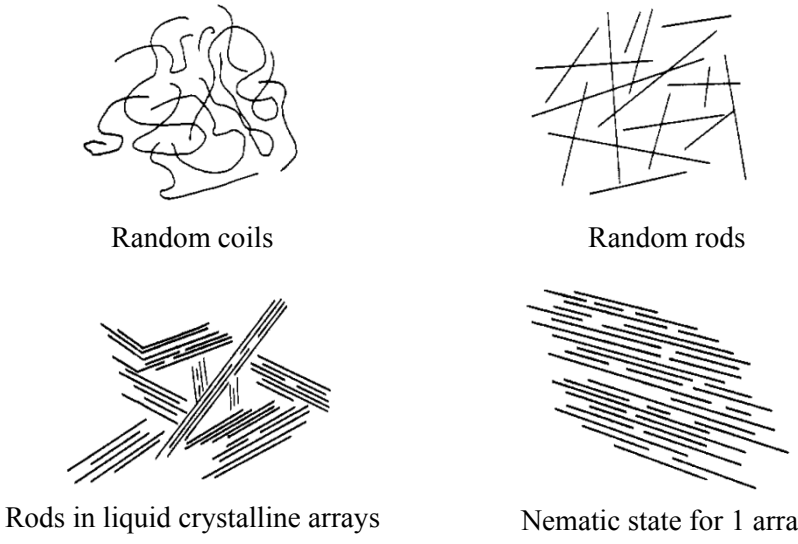



**Fig 1.3** Schematic representation of polymer states in solution.[10]

Using the strategies as noted above, much effort has been made to create

structurally modified aramids having better solubility and processability with retention of their superior thermal and mechanical properties.

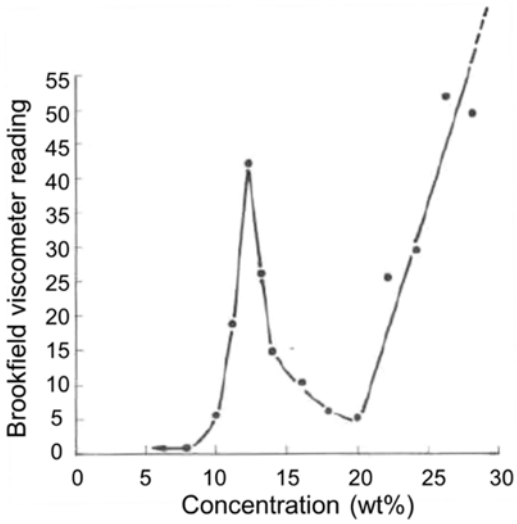



**Fig 1.4** Decrease in bulk viscosity of PPTA in sulfuric acid[12]

For example, introduction of bulky pendant group[14,15], meta or ortho linkages[16,17] and flexible moieties like ether, sulfone etc[18, 19], *N*-phenylation or methylation[20], preparation of copolymers such as poly(ester-amide)s[21,24] and poly(amide-ester-imide)s[22] resulted in a number of modified aramids. But, when flexible, ortho or meta linkage are introduced into the PPTA backbone, the polymer did not show liquid crystalline behavior any longer because the linkages obstruct the extended, trans and linear chain conformation. There is a trade-off relationship between solubility and liquid crystalline behavior. Thus, it is important that the solubility of PPTA should be improved as their conformation is not affected.

Bair, Morgan and Killian[10] reported that chlorinated PPTA (Cl-PPTA) was soluble and exhibited lyotropic behavior in DMAc + LiCl solution because

Cl-PPTA is less symmetrical than PPTA. Oh[23] et al reported that cyano PPTA (CN-PPTA) was soluble in DMAc, NMP containing alkali metal salt and the polymer formed stable liquid crystalline solution at high concentration and could be spun to high modulus fiber. Krigbaum[3] et al synthesized an aromatic polyamide using terephthalic acid having phenyl pendant group as monomer retaining the PPTA backbone and this polymer exhibited liquid crystalline behavior NMP + 4% LiCl solution also.

Amide group is considered as one of the semirigid (semiflexible) rod-like mesogenic units.[25] The C-N bond is hindered from rotation due to its double bond character. Pauling predicted a rotational energy barrier of 21 kcal/mol which corresponds to about 40% double bond character for the C-N bond of amides. The contribution of this double bond character was demonstrated by NMR studies performed on $(CH_3)_2NC(O)$-R. When R is $CH_3$-, the rotational energy barrier is 18.9 kcal/mol and decreases to 14.4 kcal/mol for R is phenyl group. Due to double bond character, its rotation is restricted and 2 conformer can be exist. In case of amide derivatives, they select trans conformer because the cis form is more unstable than trans form. This results from the steric effect.

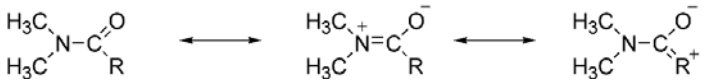


**Fig 1.5** The resonance forms of amide group[28]

The conformational behaviors of esters are very close to that of amides. Ester derivatives select trans conformation like amide. Many theoretical

calculations and experimental results suggested that the trans conformation represents the most stable structure. There is a better $O_n$-$C_{\pi^*}$ in the trans form of esters “hyperconjugation” which decreases the free energy of trans conformer. Thus, the potential energy of trans conformer is lower than the cis conformer with 7.9 kcal/mol. In the energy profile there is a hump at 90° which is due to the $O_n$-$C_{\pi^*}$ overlap which creates a double bond character on the O-C bond. This double bond character creates a configurational character for the cis and trans conformers of esters and amides and subsequently, these compounds behave close to class of rigid mesogens. Therefore, they should be classified as semirigid or semiflexible rod-like mesogens.

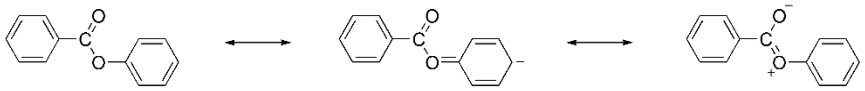


**Fig 1.6** The resonance forms of ester group[28]

In this study, aromatic diamine containing an ester group between 2 benzene rings as a mesogenic unit was designed to reduce the hydrogen bonding between the amide bonds. In addition, fluorine atom was substituted into a benzene ring as the polar substituent to increase the solubility of polymer. As noted above, because ester group is a mesogenic group and tend to have trans conformation, it is expected that the extended, linear, trans conformation of polymer backbone is not affected largely. Using the designed aromatic diamine as monomer, wholly aromatic poly(ester-amide)s were synthesized and their thermal properties, crystallinity, solubility and liquid crystalline behavior was investigated.

# Chapter 2. Experimental Section

## 2.1 Materials

All reagents were purchased from Sigma-Aldrich, Alfa-Aesar, TCI chemicals, Samchun chemical and Acros Organics and used as received. Tetrahydrofuran and methylene chloride (Samchun chemical, HPLC grade) were purified by solvent purification systems (Innovative Technology Inc, PS-Micro model) before use. *N*,*N*-Dimethylacetamide(DMAc), pyridine, fuming nitric acid (Samchun chemicals), 4-nitrophenol, 4-nitrobenzoyl chloride (Alfa Aesar) and 2-fluorophenol (TCI chemicals) were used without any further purification. *N*-Methyl-2-pyrrolidone(NMP), the polymerization solvent was anhydrous(Alfa-Aear) and calcium chloride(Alfa-Aesar) was dried under vacuum at 120 °C before use.

## 2.2 Synthesis of monomers

### 2.2.1 Synthesis of 4-Nitrophenyl-4'-nitrobenzoate (NPNB)

Scheme 2.1 shows the whole synthetic route of the comonomer, 4-aminophenyl-4-aminobenzoate (APAB). The dinitro compound, 4-nitrophenyl-4-nitrobenzoate (NPNB) was prepared by esterification of 4-nitrobenzoyl chloride with 4-nitrophenol. A solution of 50 g (0.36 mol) of 4-nitrophenol in 200 ml DMAc was stirred at 70 ℃ . To the solution 66.7 g (0.36 mol) of 4-nitrobenzoyl chloride was added in one portion. The solution was stirred at 70 ℃ for additional 3 hours. After 3 hours, the solution was

poured into 600 ml DI water, and a white precipitate appeared. The precipitate was collected by suction filtration and washed thoroughly with water. Finally, the filter cake was washed with acetone and collected by suction filtration. Before drying the product, the filter cake was pressed with spatula to remove residual liquids (water or acetone). Finally, the product was dried under vacuum at 100 °C to give compound **1** 90 g as white powder. (87% in yield)

$^1$H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, 2H), 8.34-8.39 (m, 6H)

Anal. calcd for $C_{13}H_8N_2O_6$ ($M_w$=288.04): C, 54.18; H, 2.80; N, 9.72; O, 33.31%. Found: C, 54.35; H, 2.77; N, 9.55; O, 33.33%.

IR (KBr): 3100 (aromatic ring str.), 1750 (C=O str.), 1550, 1480, 1350 ($NO_2$ str.) and 480 $cm^{-1}$ ($NO_2$ rocking)

### 2.2.2 Synthesis of 4-Aminophenyl-4'-aminobenzoate (APAB)

A 2-neck round bottom flask was charged with compound **1** (40.0 g, 0.139 mol) and stannous chloride (211g, 1.11 mol) at room temperature. 250 mL of 95% ethanol and 10 ml of concentrated hydrochloric acid were added, and the reaction mixture was heated to reflux at 80°C. As the reaction progressed, the mixture became homogeneous solution. At that time, the heat of reaction generated and the solvent, EtOH boiled very vigorously. (The reaction must be allowed to open condition, no closed system). After TLC monitoring, the solution was basified with saturated $Na_2CO_3$ solution until the pH of solution became 9~10. After the adjustment of pH, the suspension was extracted with EtOAc 3 times. The organic layer was washed with water, brine and dried($MgSO_4$). EtOAc was rota-evaporated and the crude product was recrystallizaed in EtOH to give compound **2** 23.7 g as golden yellowish white

needle-like crystal. (75 % in yield)

$^1$H NMR (300 MHz, DMSO-$d_6$): δ 4.99 (br s, 2H), 6.06 (br s, 2H), 6.55-6.63 (dd, 4H), 6.8 (d, 2H), 7.7 (d, 2H)

Anal. calcd for $C_{13}H_{12}N_2O_2$ ($M_w$=228.25): C, 68.41; H, 5.30; N, 12.27; O, 14.02%. Found: C, 68.51; H, 5.32; N, 12.19; O, 13.98%.

IR (KBr): 3400 and 3320 ($NH_2$ str.), 3070 (aromatic ring str.), 1700 (C=O str.) and 1590 $cm^{-1}$($NH_2$ def.), m.p. 186~187℃

### 2.2.3 Synthesis of 2-Fluoro-4-nitrophenol (FNP)

Scheme 2.2 shows the whole synthetic route of the desired monomer, 2-fluoro-4-aminophenyl-4'-aminobenzoate (FAPAB). First, 2-fluorophenol was nitrated using fuming nitric acid as the nitrating agent and then, the nitrated phenol derivative was esterified with 4-nitrobenzoyl chloride to make a dinitro compound. Finally, the dinitro compound was reduced to diamine using stannous(II) chloride as the reducing agent. FNP was prepared following the U.S. patent.[26] To a stirred solution of 2-fluorophenol 29.28 g (0.261 mol) in dichloromethane 200 ml which was cooled to −10℃(ice + dry ice + acetone bath), was slowly added 95% fuming nitric acid (19.66 g, 0.287 mol, 1.1 equiv) over a 1 hour period. During the addition, the temperature was maintained at about −5℃ monitored by thermometer. After the addition of nitrating agent was complete, stirring was continued at 0℃ for an additional hour. At the end of this period, the nitrated product which had formed was filtered and washed with several portions of cold water. This filtrate was taken up in ether or EtOAc, washed with concentrated hydrochloric acid, water,

brine and dried ($MgSO_4$) and the solvent was evaporated. The yellowish crude product appeared. This crude product was recrystallized from toluene to give 16.41 g of a light yellow crystal (40 % in yield). NMR (DMSO-$d_6$) showed this to be the desired the nitrated product 2-fluoro-4-nitrophenol.

$^1$H NMR (300 MHz, DMSO-$d_6$): δ 7.09 (tr, 1H), 7.95 (dddd, 1H), 8.04 (dd, 1H), 11.58 (br s, 1H).

### 2.2.4 Synthesis of 2-Fluoro-4-nitrophenyl-4-nitrobenzoate (FNPNB)

A 2-neck round bottom flask was charged with 2-fluoro-4-nitrophenol (28 g, 0.178 mol), pyridine (14.1 g, 0.178 mol) in dry THF under Ar atmosphere. The flask was placed in ice + acetone bath. After 15 minutes, 4-nitrobenzoyl chloride 33 g (0.178 mol) was added in one portion and then, the mixture was stirred. After 1 hour, the reaction was allowed to room temperature for additional 3 hours. After 3 hours, THF was evaporated and the resulting solid was taken up in hot EtOAc. The organic layer was washed concentrated hydrochloric acid, water, brine and dried ($MgSO_4$). The solvent was rota-evaporated and the crude product was recrystallized from EtOH or EtOH + EtOAc (5:1) to give 48.5 g of yellow solid. (89% in yield)

$^1$H NMR (300 MHz, $CDCl_3$-*d*): δ 7.52 (1H), 8.13 (2H), 8.40-6.63 (4H)

Anal. calcd for $C_{13}H_7FN_2O_6$ ($M_w$=306.20): C, 50.99; H, 2.30; F, 6.20; N, 9.15; O, 31.35%. Found: C, 51.06; H, 2.35; F, 6.08; N, 9.15; O, 31.36%.

IR (KBr): 3100 (aromatic ring str.), 1760 (carbonyl str.), 1490 ($NO_2$ antisym str.) and 1345 $cm^{-1}$ ($NO_2$ sym str.)

### 2.2.5 Synthesis of 2-Fluoro-4-aminophenyl-4'-aminobenzoate (FAPAB)

A mixture consisting of 30 g (0.098 mol) of FNPNB, 149 g (0.784 mol, 8 equiv, $M_w$= 189.62) of stannous(II) chloride or 176.9 g (0.784 mol, 8 equiv, $M_w$= 225.65) stannous(II) chloride dihydrate and 200 ml of 95% EtOH was put into a round bottom flask[27], with stirred while 5 ml of concentrated hydrochloric acid was added slowly. After addition of hydrochloric acid was finished, the mixture was heated to 70℃. After a few minutes, the suspension became homogenous solution. At that time, the heat of reaction generated and the solvent, EtOH boiled very vigorously. (The reaction must be allowed to open condition, no closed system). After TLC analysis, the reaction solution was poured into 150 ml DI water and the mixture was basified with saturated $K_2CO_3$ solution. After the adjustment of pH, the suspension was extracted with EtOAc 3 times. The organic layer was washed water, brine and dried ($MgSO_4$). EtOAc was rota-evaporated and the residual solid was recrystallized from EtOH to give 20 g of yellow needle-like crystal. (83% in yield)

$^1$H NMR (300 MHz, $CDCl_3$-*d*) δ 3.69 (br s, 2H), 4.12 (br s, 2H), 6.42 (2H), 6.66 (d, 2H), 6.94 (tr, 1H), 7.98 (d, 2H)

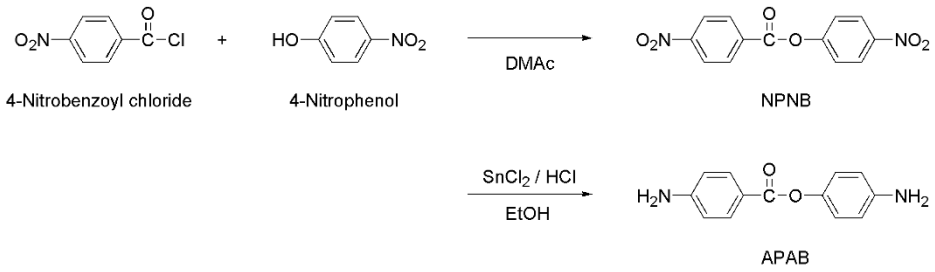
Anal. calcd for $C_{13}H_{11}FN_2O_2$ ($M_w$=246.24): C, 63.41; H, 4.50; F, 7.72; N, 11.38; O, 13.00%. Found: C, 63.38; H, 4.56; F, 7.62; N, 11.34; O, 13.10%.

IR (KBr): 3400 and 3320 ($NH_2$ str.), 1715 (C=O str.) and 1600 $cm^{-1}$($NH_2$ def.), m.p. 190℃

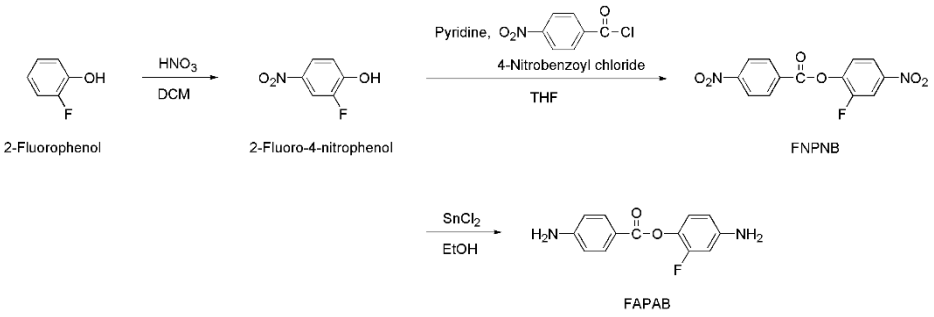
### 2.2.6 Synthesis of poly(ester-amide)s

Wholly aromatic poly(ester-amide) was prepared by low-temperature polycondensation of terephthaloyl chloride (TPC) and the synthesized aromatic diamines. Scheme 2.3 shows the polymerization route of poly(ester-amide)s. The polymerization solvent and metal salt was *N*-methyl-2-pyrrolidone(NMP) and calcium chloride ($CaCl_2$), respectively. Calcium oxide (CaO) was used as the neutralizing agent to neutralize HCl formed during the polymerization. The stirring rate was fixed at 300 rpm. The preparation of wholly aromatic poly(ester-amide)s was described as the general procedure. To a 500 mL, 3-necked round bottom flask equipped with a mechanical stirrer and Ar inlet/outlet tube, NMP 41.26 g (monomer concentration 7.3 wt%)was added and $CaCl_2$ 0.8252 g (2 wt% of NMP) was dissolved in NMP. After the dissolution of $CaCl_2$, aromatic diamine FAPAB 3 g (0.0122 mol) was added and dissolved. (Depending on the polymerization condition, pyridine was added.) When the aromatic diamine was fully dissolved in NMP + $CaCl_2$ solution, the flask was placed in acetone + ice bath. After 10 minutes, TPC 2.473 g (0.0122 mol) was added in one portion and the reaction mixture was stirred vigorously at 300 rpm. After a few minutes, the reaction mixture became gel, solution, or solid depending on the polymerization condition. In case of not using the neutralizing agent, 500 ml DI water was poured into the reaction flask and the synthesized polymer was precipitated. The precipitated polymer was collected by suction filtration. The filtrate was pulverized by mixer and washed with hot and cold water 2 times to extract solvent, metal

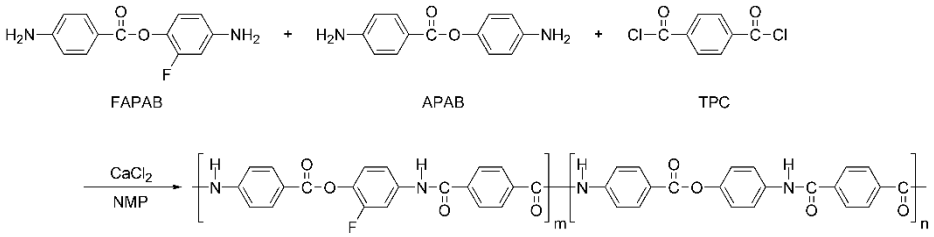
salt and HCl. Finally, obtained polymer precipitate was washed with acetone thoroughly, collected by suction filtration and dried under vacuum at 100℃ for 24 hrs. In case of neutralizing the polymer dopes, the neutralizing agent, CaO 0.6832 g (equimolar amount to diamines) was added. The mixture was well-mixed to make the neutralizing agent percholate into the solidified polymer solution. The reaction mixture became solution, solid or gel after the neutralization depending on the polymerization condition.




**Scheme 2.1** The whole synthetic route of 4-aminophenyl-4'-aminobenzoate (APAB)




**Scheme 2.2** The whole synthetic route of the desired monomer, 2-fluoro-4-aminophenyl-4'-aminobenzoate (FAPAB)




**Scheme 2.3** The polymerization route of poly(ester-amide)s

**Table 2.1** Synthesized aromatic poly(ester-amide)s

| Polymer name | Feed ratio (%) | |
|---|---|---|
| | FAPAB | APAB |
| F 100 | 100 | 0 |
| F 75 | 75 | 25 |
| F 50 | 50 | 50 |
| F 25 | 25 | 75 |
| F 0 | 0 | 100 |

## 2.4 Characterization

The chemical structures of the materials used in this study were identified by $^{1}H$ NMR (Avance DPX-300) and $^{13}C$ NMR (Avance DPX-500). Elemental analyses were conducted with Flash1112, Flash2000 model and quantified with TCD detector in dynamic flash combustion method. The identification of functional groups was carried with FT-IR (Thermo Scientific, Nicolet 6700). The spectra of solids were obtained using KBr pellet. The vibrational transition frequencies are reported in wavenumbers ($cm^{-1}$).

The liquid crystalline behaviors of the polymer solution were observed by Brookfield viscometer and polarized optical microscopy (POM). The bulk viscosity of polymer dopes was measured by Brookfield viscometer (FUNGILLAB S.A./VISCO STAR-R model) using spindle No.5 at 10 rpm under room temperature. The optical anisotropy of polymer solution was observed by POM.

Thermogravimetric analyses were carried out with TGA 2050 Thermogravimetric Ananlyzer model (TA instrument) at a heating rate of 10℃/min under a $N_2$ atmosphere. The thermal transition temperatures were determined by a differential scanning calorimeter (DSC 2920, TA instrument). In DSC analyses, the heating and cooling rate were fixed with 10℃/min. The optimized geometries of monomers and repeating units were obtained by density functional theory (DFT) calculation method using B3LYP functional and 6-31G basis set. The crystallinity of aromatic poly(ester-amide)s were investigated by XRD in powder state and the scan range was from 0˚to 50˚.

## 2.5 Measurement of viscosities

The molecular weights of synthesized polymers were determined from intrinsic viscosity [ $\eta$ ]. To obtain the intrinsic viscosity, relative viscosity have to be measured first.

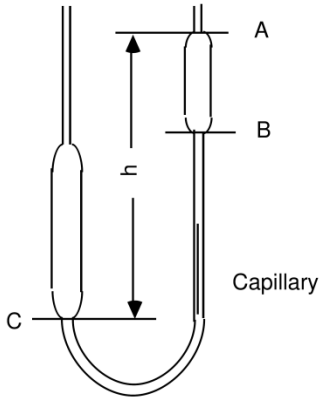



**Fig 2.1** Simple viscometer

The experiment is to fill the viscometer such that the level on the left side is at point C and the level on the right side is at point A. Sample solution should be dilute solution. The flow time of pure solvent ($t_0$) and polymer solution (t) were measured and compared each other.

1. Relative viscosity $\eta_{rel} = \frac{t}{t_r}$

2. Specific viscosity $\eta_{sp} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$

3. Inherent viscosity $\eta_{inh} = \frac{ln\, \eta_{rel}}{c}$

4. Intrinsic viscosity $[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \frac{\ln \eta_{rel}}{c}$

$\eta_{inh}$ is inherent viscosity, $\eta_{rel}$ is relative viscosity (the ratio of the viscosity or the flow time of a solution to the viscosity or the flow time of the pure solvent used) and $c$ is the concentration of the polymer solution. The dried polymer were dissolved in NMP + 6wt% $CaCl_2$ (polymer concentration= 0.5 g/dL) and then, inherent viscosities were measured using Cannon Fenske viscometer at 30℃. After that, the obtained inherent viscosities were plotted against several dilute concentration. From this plot, intrinsic viscosities were obtained by extrapolating to zero concentration finally.

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \frac{\ln \eta_{rel}}{c}$$

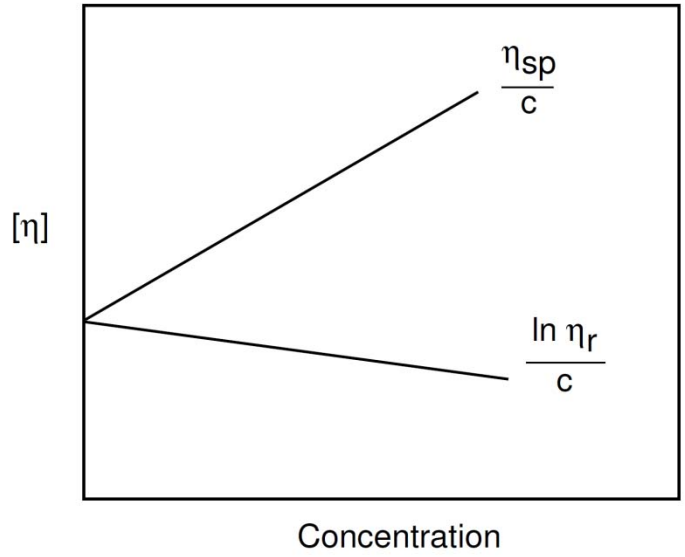



**Figure 2.2** Extrapolation of inherent viscosity to zero concentration

# Chapter 3. Results and Discussion

## 3.1 Synthesis and Characterization

The chemical structures of 4-nitrophenyl-4'-aminobenzoate (NPNB), 4-aminophenyl-4'-aminobenzoate (APAB), 2-fluoro-4-nitrophenol (FNP), 2-fluoro-4-nitrophenyl-4'-nitrobenzoate (FNPNB), 2-fluoro-4-aminophenyl-4'-aminobenzoate (FAPAB) are are identified by $^1$H NMR, as shown in Figure 3.1-5, respectively.

In case of synthesis of NPNB in small scale, low boiling point solvent like THF, acetone could be used and a normal material purification (extraction, recrystallization) was applicable in this synthesis. But, it was hard to collect the recrystallized NPNB due to its very big volume. For this reason, to scale-up the reaction, the work-up of NPNB was made up of precipitation and washing instead of recrystallization. Polar aprotic solvent, DMF, DMAc or NMP were used the reaction solvent to facilitate the $S_N2$ reaction of phenol and acid chloride. Especially, DMAc was used due to the miscibility with water. $^1$H NMR and elemental analysis shows that this procedure is a good alternative in this type reaction. In case of synthesis of APAB, $SnCl_2$ was the best reducing agent. The heat of reaction was generated very vigorously. So, this reaction was allowed to open to air in the fume hood.

When FNP were synthesized, many nitrating agents were applied. For example, 70% $HNO_3$, $HNO_3$ + $H_2SO_4$ mixture, $NaNO_2$ etc were used to nitrate 2-fluorophenol. But, the reaction using these nitrating agents resulted in dinitro compound and it is impossible to mono-nitrate at *p*-position of OH

in 2-fluorophenol. But, the reaction using 95% fuming nitric acid as the nitrating agent and dichloromethane as solvent resulted in the desired product, 2-fluoro-4-nitrophenol following the procedure US patent 4750931. In this reaction, the low temperature under −10℃ should be maintained and the product was recrystallized from toluene instead of methyl cyclohexane mentioned in the patent. In case of synthesis of FNPNB, it did not have any problems as NPNB. So it was synthesized generally using common solvent. The reduction procedure of FNPNB was same as NPNB. $^{1}$H NMR spectra, FT-IR spectra (Fig 3.1~3.7) shows that NPNB, APAB, FNP, FNPNB and FAPAB were successfully synthesized.

In table 3.1, there are elemental analyses results of NPNB,APAB, FNPNB and FAPAB showing that the calculated values of content of C,H,N,O,F is almost same as the obtained value from elemental analyses. From the dinitro compounds to the diamines, the weight content of oxygen decreased and the weight content of hydrogen increased. From this, the diamines with high purity were synthesized

Using these diamines, aromatic poly(ester-amide)s were successfully synthesized. The intrinsic viscosities (I.V. value) of the polymers are higher than 8 except for APAB based homopolymers. Considering that the generally the I.V. value of PPTA is 5~6, high molecular weight of aromatic poly(ester-amide)s were obtained. The functional groups of aromatic poly(ester-amide)s were identified by FT-IR in fig 3.8.

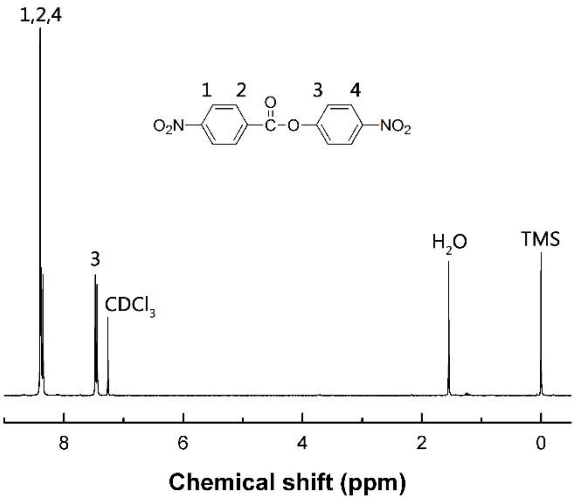



**Figure 3.1** Chemical structure and $^{1}$H NMR spectrum of NPNB

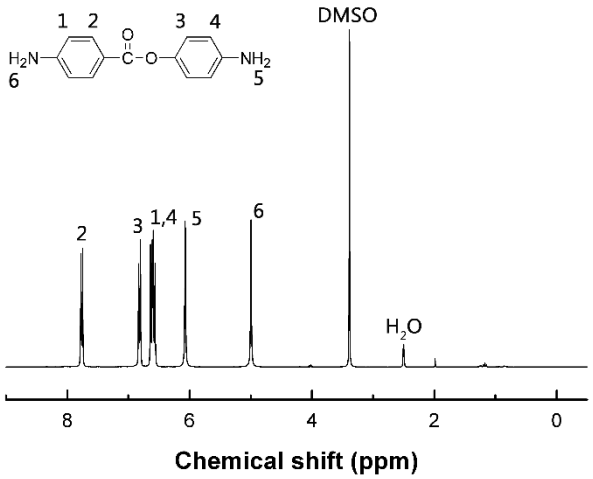



**Figure 3.2** Chemical structure and $^{1}$H NMR spectrum of APAB

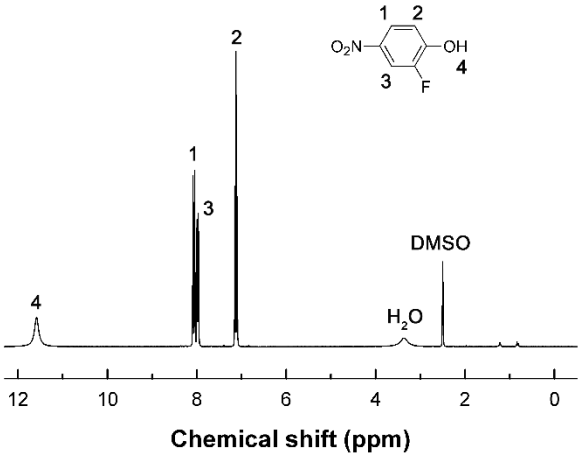



**Figure 3.3** Chemical structure and $^1$H NMR spectrum of FNP

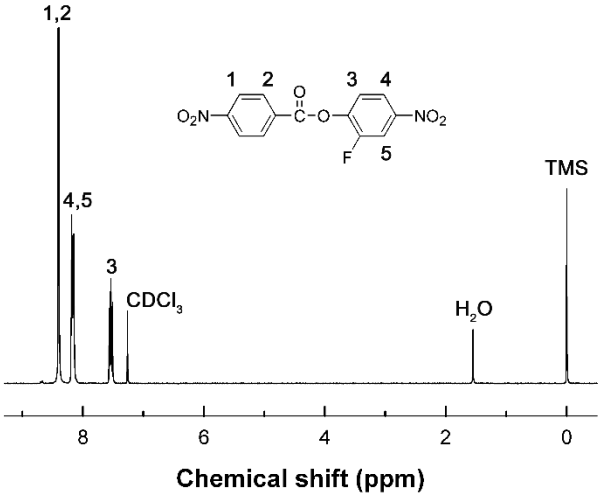



**Figure 3.4** Chemical structure and $^1$H NMR spectrum of FNPNB

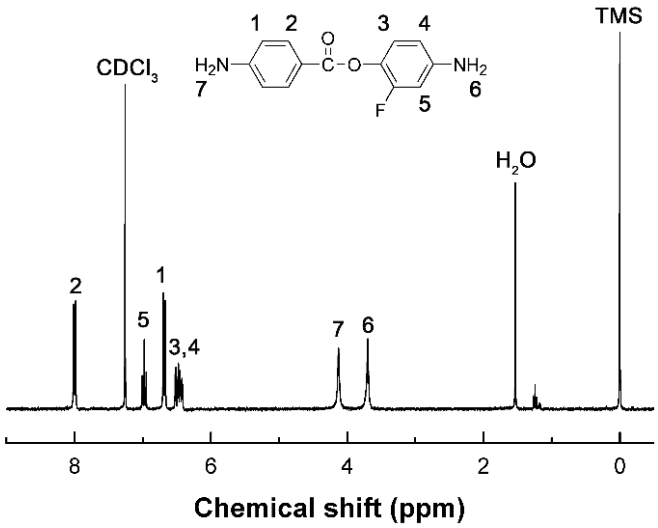



**Fig 3.5** Chemical structure and $^{1}H$ NMR spectrum of FAPAB

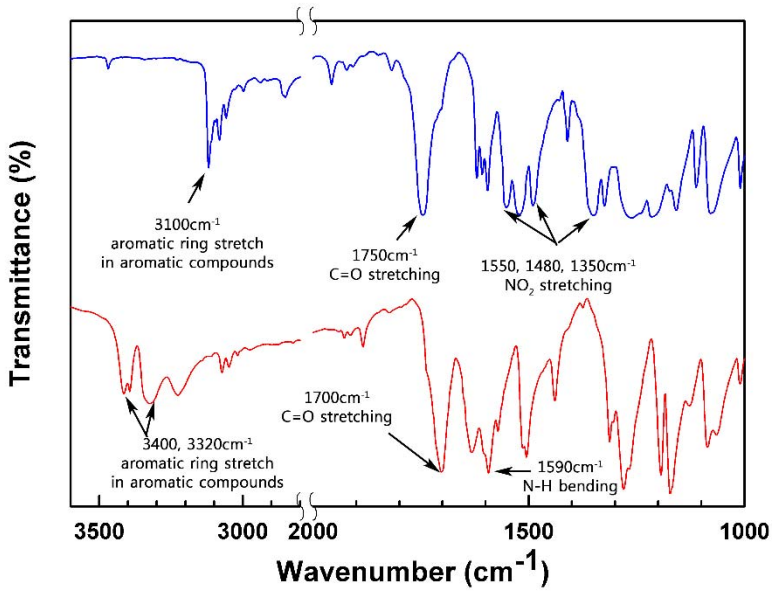



**Fig 3.6** FT-IR spectrum of NPNB(blue) and APAB(red)

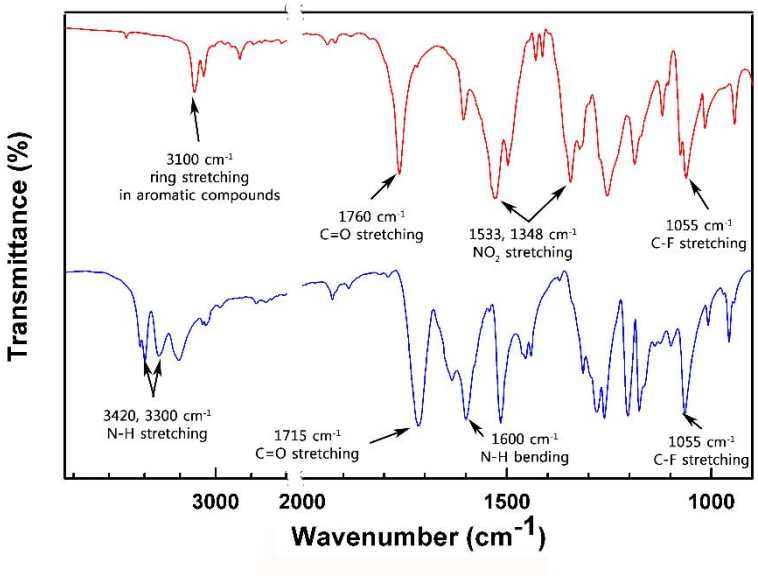



**Fig 3.7** FT-IR spectrum of FNPNB(blue) and FAPAB(red)

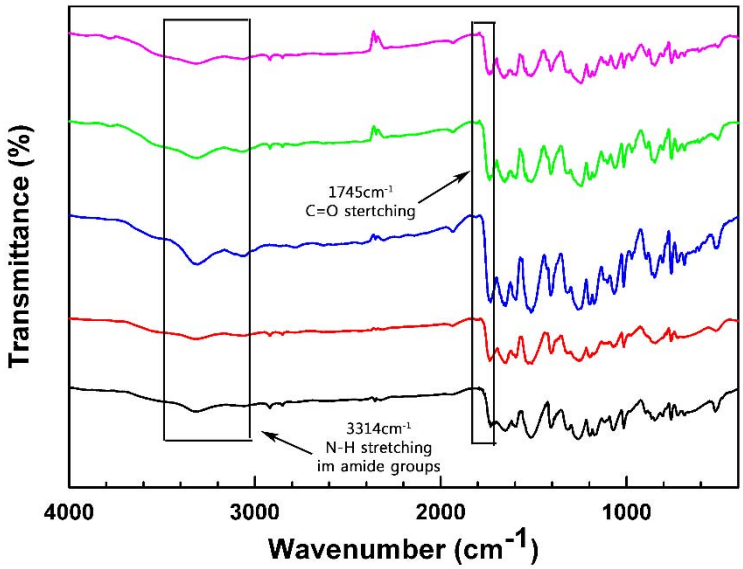
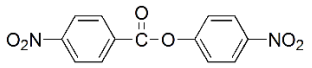
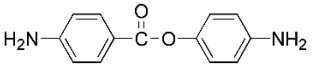
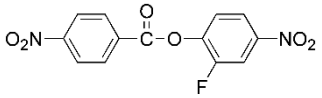
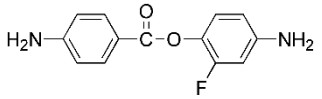



**Fig 3.8** FT-IR spectrum of poly(ester-amide)s; F0(black), F25(red), F50(blue), F75(green), F100(pink)

**Table 3.1** Results of elemental analyses of NPNB, APAB, FNPNB and FAPAB.

| Chemical structure | Formula | | C (wt%) | H (%) | N (wt%) | O (wt%) | F (wt%) |
|---|---|---|---|---|---|---|---|
|  | $C_{13}H_8N_2O_6$ | Calc. | 54.18 | 2.80 | 9.72 | 33.31 | - |
| | | Found. | 54.35 | 2.77 | 9.55 | 33.33 | - |
|  | $C_{13}H_{12}N_2O_2$ | Calc. | 68.41 | 5.30 | 12.27 | 14.02 | - |
| | | Found. | 68.51 | 5.32 | 12.19 | 13.98 | - |
|  | $C_{13}H_7FN_2O_6$ | Calc. | 50.99 | 2.30 | 9.15 | 31.35 | 6.20 |
| | | Found. | 51.06 | 2.36 | 9.15 | 31.36 | 6.08 |
|  | $C_{13}H_{11}FN_2O_2$ | Calc. | 63.41 | 4.50 | 11.38 | 13.00 | 7.72 |
| | | Found. | 63.38 | 4.56 | 11.34 | 13.10 | 7.62 |

[a] The oxygen content was calculated from C,H,N elemental analysis. (wt % of O= 100 – wt% of C – wt% of H – wt% of N)
[b] The fluorine content was calculated from C,H,N and O elemental analysis. (wt % of F= 100 – wt% of C – wt% of H – wt% of N – wt% of O)

## 3.2 Optimized geometries

The optimized geometries of monomers and repeating units of polymers were obtained by DFT calculation using by density functional theory (DFT) calculation method using B3LYP functional and 6-31G basis set. Fig 3.10 shows the optimized structures of the diamines, APAB and FAPAB. The 2 benzene rings bound to ester group in APAB and FAPAB, their planarity was maintained. Thus, these monomers were expected not to disturb the conformation and only reduce the hydrogen bonding density. So, the polymer from these aromatic diamines was expected to show the liquid crystalline behavior like PPTA. Fig 3.11 shows the optimized structure of repeating units of APAB and FAPAB based homopolymers, respectively. Because it is hard to investigate many repeating unit, one repeating unit was investigated and methyl groups were attached at the end of the repeating unit for termination. Although there was a torsion between amide group and benzene ring, the moiety of the ester monomer was nearly planar in both APAB (0.3˚)and FAPAB(0.4˚). In FAPAB based homopolymer, the torsional angle of $C_1$-$C_2$-O-$C_3$ was 0.4˚and $C_4$-N-$C_5$-$C_6$ was 2.6˚. In case of APAB based homopolymer, the torsional angle of $C_1$-$C_2$-O-$C_3$ was 0.3˚and $C_4$-N-$C_5$-$C_6$ was 3.5˚.

In PPTA polymer, when the trans conformation of backbone is interrupted, their liquid crystalline behaviors disappear because of the loss of extended chain conformation of backbone. For example, when the amide hydrogen is substituted for phenylene or alkyl group, the trans conformation change into cis conformation. In acetanilide, this phenomenon have been reported[25,26,27].

Benzanilide exists exclusively in the trans conformation both in the crystal and in solution, whereas *N*-methyl benzanilide exists predominantly in the cis structure. In the $^{1}H$ NMR spectrum of *N*-methyl benzanilide in $CD_2Cl_2$, a major peak and a minor peak of the *N*-methyl group are observed below 233K, and they coalesce at 233K. In case of *N*- phenylation, Kakimoto[35] et al synthesized a aromatic polyamide using *N*,*N*'-diphenyl-*p*-phenylenediamine as monomer. The solubilities in organic solvents were greatly increased, but their mechanical properties were not good showing 46~51 MPa of tensile strength, 1.7~1.9 GPa of tensile modulus. The case of *N*-methylaion of PPTA is same as that of *N*-phenylation. Nosova[6] et al expected the conformation and equilibrium rigidity of poly-*N*,*N*'-dimehtyl-*p*-phenyleneterephthalamide from experimental results and theoretical calculations. They reported that the methylation resulted in the short length of Kuhn segment (1/20 of unsubstituted aromatic polyamide) and the conformation of polymer is coiled and non-coplanar. So, there was no liquid crystalline behavior in *N*-methylated or phenylated aromatic polyamides. As noted before, the ester group is a semirigid rod-like group and its charecteristics is similar to amide group. The rotation of ester group is hindered because of its double bond character like amide group.[31]

From this, it is expected that ester group do not disturb largely the conformation of aromatic polyamide backbone and as shown fig 3.9, the ester group only will reduce the hydrogen bonding density between the polyamide backbone.

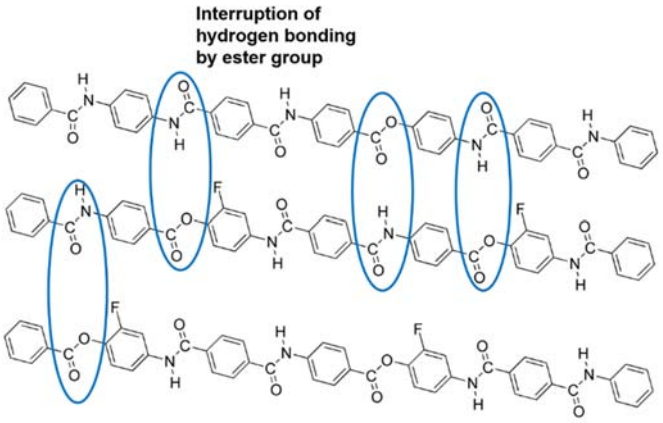



**Fig 3. 9** Hydrogen bonding of poly(ester-amide)s backbone

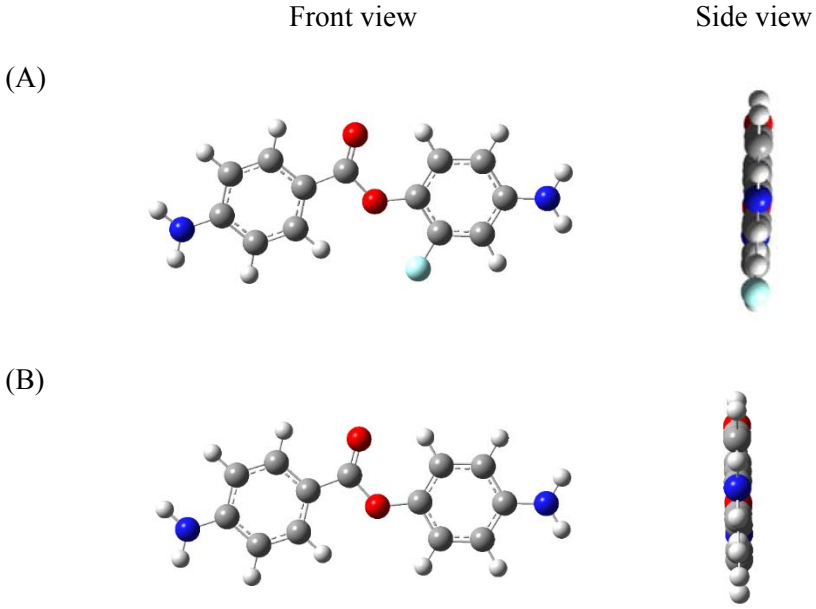



**Figure 3.10** The optimized structures of FAPAB (A) and APAB (B)

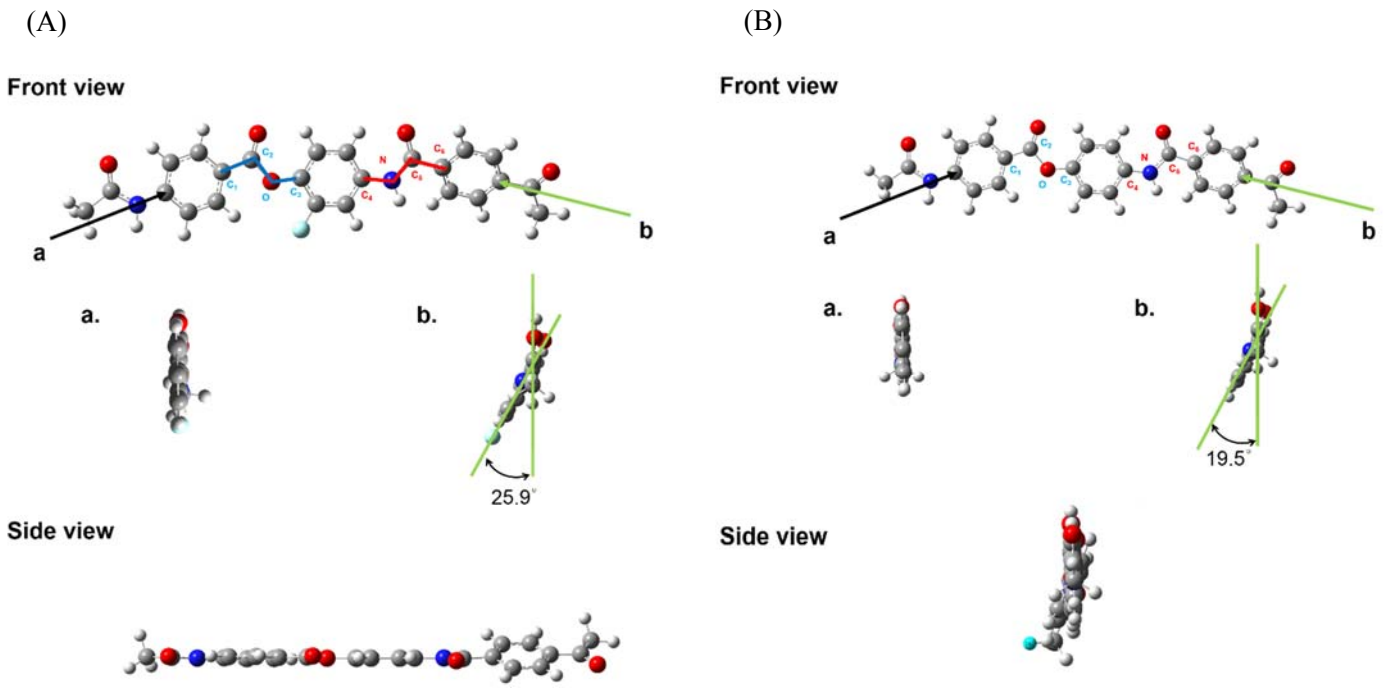



**Fig 3.11** The optimized structures of repeating unit of FAPAB (A), APAB (B) based poly(ester-amide)s (The methyl group is attached to amide groups for termination)

## 3.3 Thermal properties and crystallinity

The thermal properties and crystallinity of the monomers and polymers were investigated by TGA, DSC and XRD. As shown fig 3.12, the synthesized aromatic poly(ester-amide)s showed 2 major peak at $2\theta = 20.2^\circ$ and 22°, which well correspond the results of other studies and their crystallinity is similar to poly(*p*-phenyleneterephthalamide).(fig 3.12)[33,34]. The aromatic diamines, were degraded thermally at around 300℃ as shown fig 3.13. FAPAB and APAB showed a sharp endothermic (192, 187℃ respectively) and exothermic peak (143, 152℃ respectively) corresponding melting and crystallization in DSC thermograms (fig 3.14). This indicated that the monomers have high crystallinity. Although the degradation of fluorinated diamines earlier, the final char yield was higher than APAB and the degradation occurred through several steps. It is considered that because halogen atom (fluorine) have flame-retardant nature. Fig 3.15 shows the TGA and DTG curves of polymers. All poly(ester-amide)s had good thermal stability without any significant weight loss up to 400℃ under $N_2$ atmosphere. One thing to note is that the more fluorine content, the higher the char yield. From DTG curves, the beginning of the degradation occurred at lower temperature in the polymer having more fluorine content, but their degradation rates became slower. In DSC analysis, all the polymers did not shows any transition.

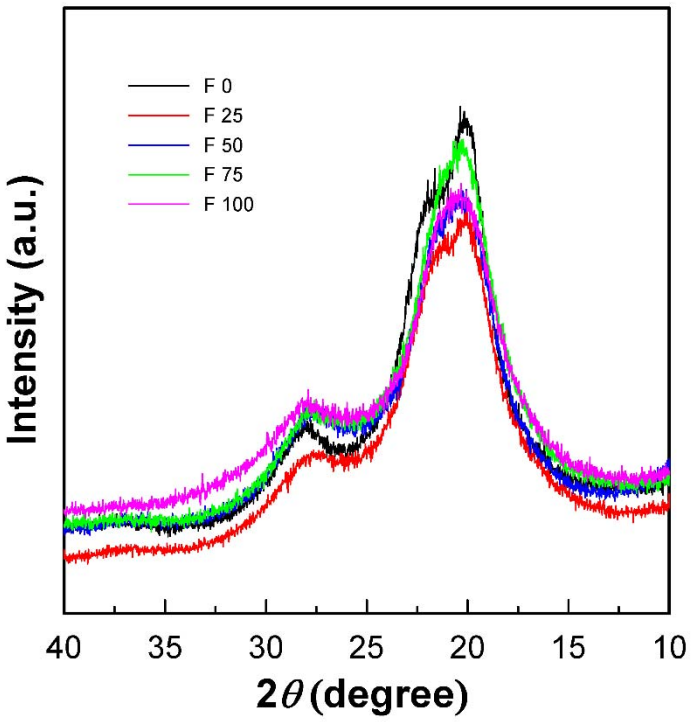
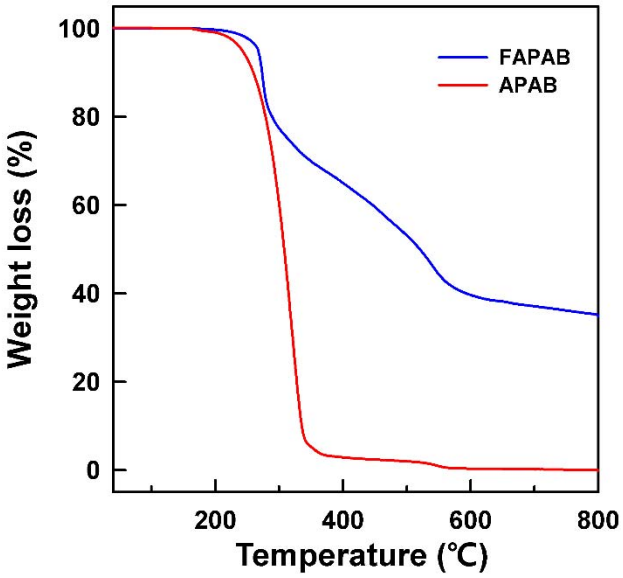



**Figure 3.12** XRD patterns of aromatic poly(ester-amide)s

(A)




(B)

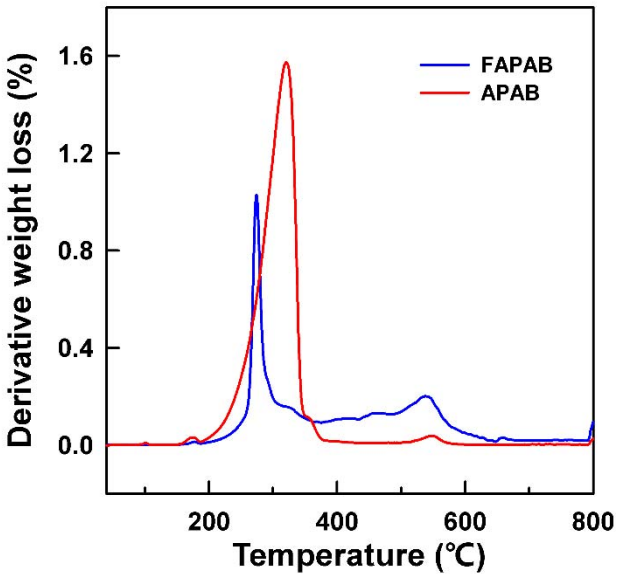
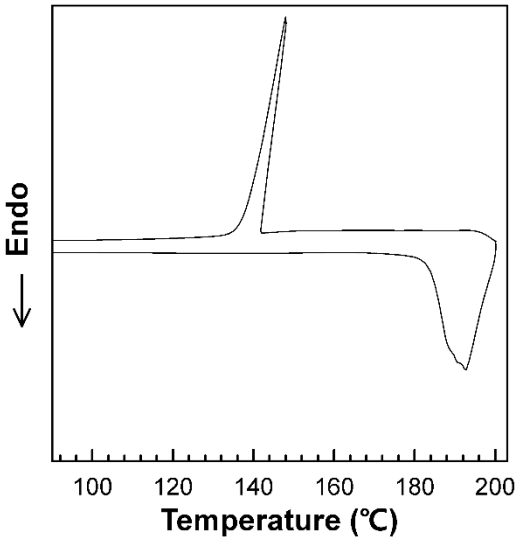



**Fig. 3.13** TGA(A)and DTG(B) thermograms of FAPAB and APAB

(A)




(B)

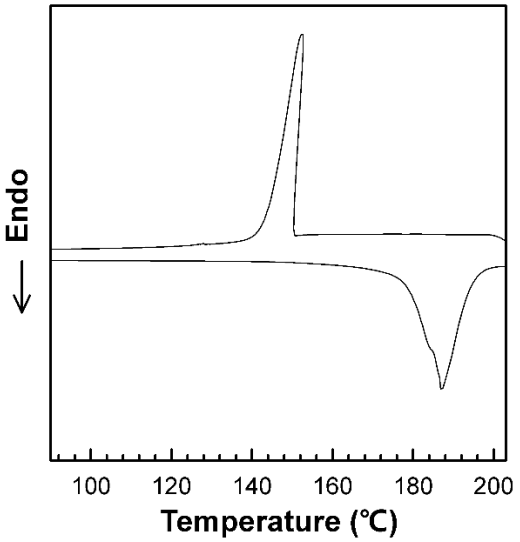
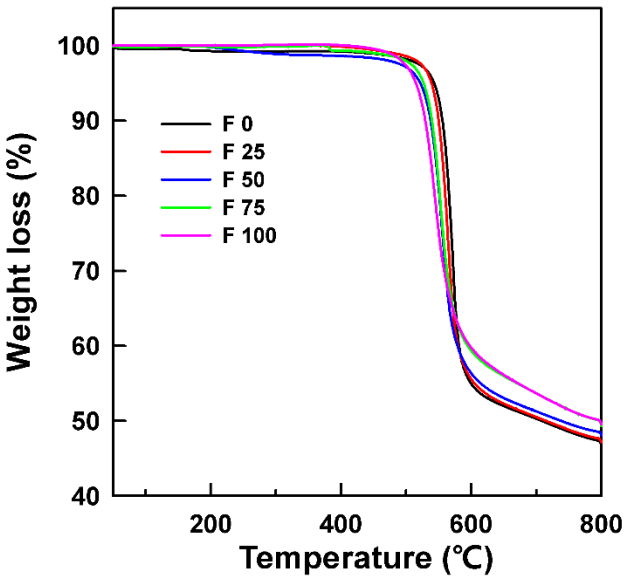



**Fig. 3.14** DSC thermograms of FAPAB(A) and APAB(B)

(A)




(B)

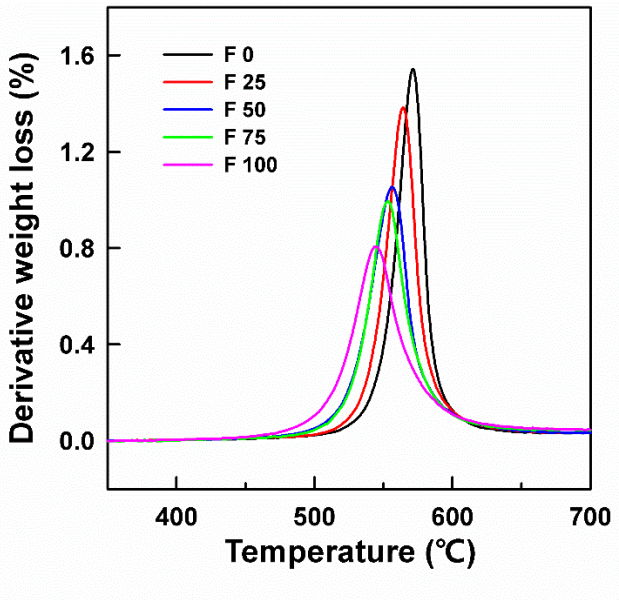



**Fig 3.15** TGA(A) and DTG(B) thermograms of poly(ester-amide)s

## 3.4 Polymerization conditions and solubility

To investigate effect of monomer concentration, temperature and time, concentration of metal salt, acid acceptor, TPC feed ratio and the ratio of 2 aromatic diamines (FAPAB and APAB) on the molecular weight of polymer, the polymers were synthesized under various condition and after that, the I.V values were measured and compared each other. Oh[31,32] et al reported that the low molecular weight of aromatic polyamides were obtained when TPC was added slowly. This indicates that the reaction of TPC with diamine is very fast and the molecular weight of aromatic polyamide is largely affected by the stoichiometric amount of TPC participating in the polymerization at the beginning of the polymerization. Also, Gulrich et al reported that rapid addition of monomers resulted at the beginning of the polymerization resulted in high molecular weight and narrow molecular weight distribution, Thus, when TPC was added, it was added in one portion rapidly. After TPC was added, the polymer solution became high viscous gel or solid above 8wt%. At that time, CaO was used to neutralize HCl generated during the polymerization ($CaO + HCl \rightarrow CaCl_2 + H_2O$). $CaCl_2$ generated by the neutralization increase the concentration of metal salt in the system, which enhance the solubilizing ability of solvent. Thus, the solidified polymer dope could be solution, gel or solid after the neutralization depending on the polymerization conditions. In all polymerization condition, CaO was used. (The addition of CaO after the solidification of polymer solution did not affect the I.V of polymers).

First, effect of monomer concentration on I.V.( [$\eta$]) values was investigated. In this case, only FAPAB was used as the diamine monomer. As shown fig. 3.16, the highest molecular weight of polymers were obtained at 9~13wt%. Except for 9~13wt%, low molecular weight polymers were obtained, relatively. It has been known that the growth of polymer chain is suppressed due to the rapid gelation and the limitation of solubilizing power of solvent at high concentration.[23,30,31,33] Also, the high concentration of monomers results in rapid gelation of polymer solution before the polymer have high degree of polymerization and the rate of side reaction become fast due to the increase of the heat of reaction resulting from the high concentration of monomers, which contribute to the low degree of polymerization. While the monomer concentration is low, the amount of polymerization solvent is excess compared with the monomers. Thus, there can be a side reaction of diacid chloride with the amide solvent (NMP, DMAc) and competition between solvents and diamines, which result in relatively lower molecular weight polymers. This results well corresponded the experimental results of Morgan[10,11] et al, Kim[33,34] et al, Oh[31,32] et al. Second, effect of temperature on molecular weight was investigated at −10, 20, 35, 50, 70℃ respectively. As shown fig 3.17, temperature did not affect the molecular weight of the polymers. Morgan[33] et al reported that when the solution polycondensation of diamine monomers like *p*-phenylenediamine (PPD) with diacid chloride occur, low temperature resulted in high molecular weight polymers. Because the oxidation of diamine was suppressed at low temperature. But, in this study, high molecular weight of polymers were obtained at high temperature. It was considered that the

enhanced oxidation stability resulted in the high molecular weight of polymer at high temperature because the thermal stability t of FAPAB is higher than PPD relatively.

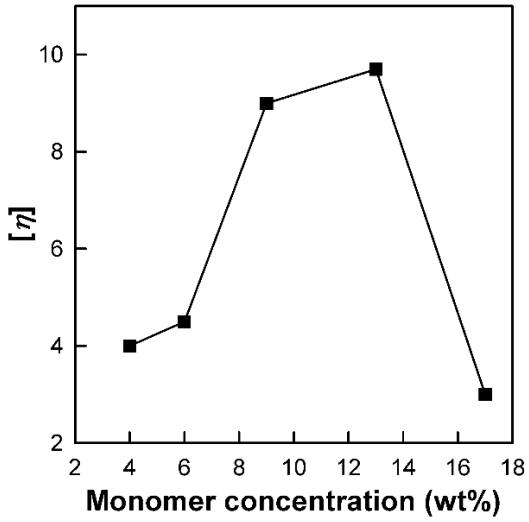



**Figure 3.16** Effect of monomer concentration on I.V (metal salt: 2%)

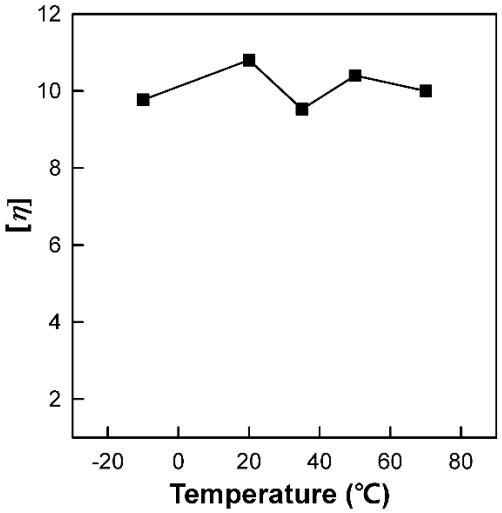



**Figure 3.17** Effect of temperature on I.V (metal salt: 2%, monomer concentration: 13wt%)

The effect of metal salt were investigated also. Generally, when the metal salt is used, the metal salt forms complex with amide solvent like DMAc, NMP, which results in greatly enhanced solubilizing ability. LiCl, $CaCl_2$ is used as the metal salt usually in the preparation of aromatic polyamides. This complex stabilize the polymerization intermediate, which results in the high degree of polymerization.[34]

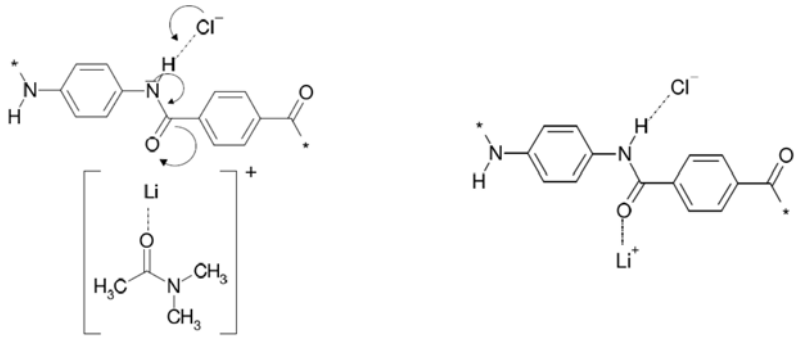



**Fig 3.18** Complexation of LiCl with DMAc[37]

As shown fig 3.18, metal salt can form complex with amide solvent. Left is complex at low concentration and right is at high concentration of metal salt. At low concentration, the anion is bound to amide proton and the cation interact with lone pair electron of carbonyl oxygen in amide solvent. This was proven by FT-IR and NMR in the previous work. The amide proton peak was shifted to downfield in NMR and the new C=O band appeared in IR due to $Li^{+}\cdots O{=}C$ interaction[45]. In this case, because the hydrogen bonding of polymer backbone is interrupted and the salt-solvent complex can interact with the polymer chain more favorably than the pure solvent, the solubility of solvent is enhanced. But, at high concentration of metal salt, the cation

interact with the carbonyl oxygen in amide of polymer backbone directly than the carbonyl oxygen of solvent. Thus, the solubility of solvent to polymer is not enhanced effectively. Gopal et al and Diorio et al supported the mechanism in their studies[46,47]. NMP + $CaCl_2$ system is similar to DMAc + LiCl

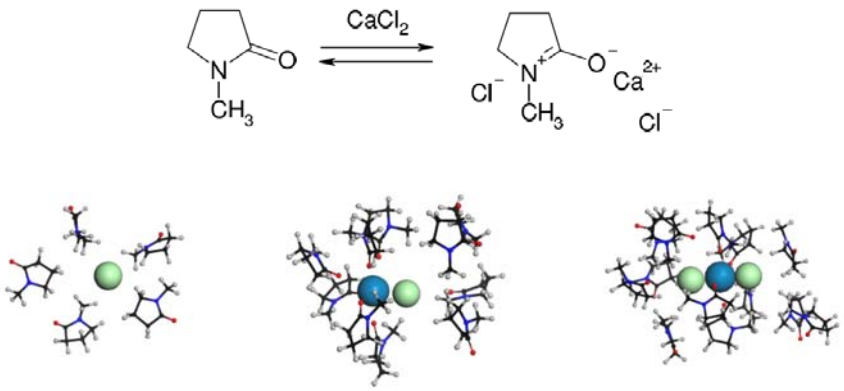



**Fig 3.19** Complexaton of NMP with $CaCl_2$ ($Cl^-$ shown in green, $Ca^{2+}$ shown in blue)[37]

Thus, there can be an optimum amount of metal salt when the metal salt is used in the polymerization. Fig 3.20 shows the effect of concentration of $CaCl_2$ on the I.V. Since the solubility of $CaCl_2$ in NMP is only 6% at 20℃, this experiment was carried up to 5% of $CaCl_2$. When 1% of calcium chloride was added, I.V of the polymer was 7.08. But, when 2% of $CaCl_2$ was added, there was an increase in I.V up to about 10. In case of 3% and 4% addition of $CaCl_2$, there was not marked increase in I.V of polymer. When 5% of $CaCl_2$ was added, I.V value dropped with about 8. Thus, the optimum amount of $CaCl_2$ was 2%.

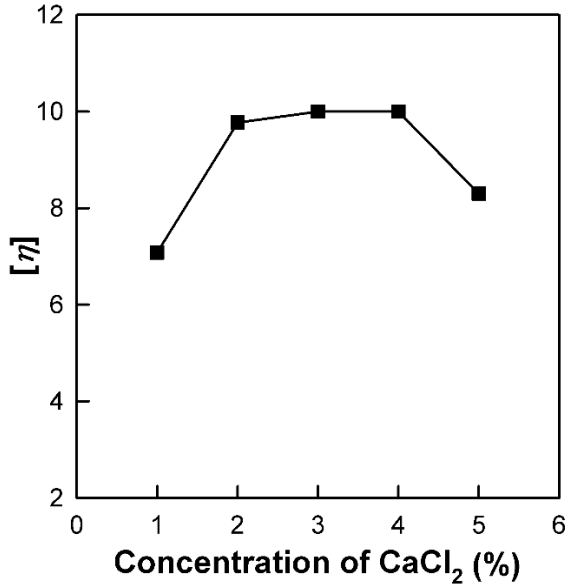



**Fig 3.20** Effect of concentration of $CaCl_2$ on I.V (monomer concentration: 13wt%, temperature: −10℃).

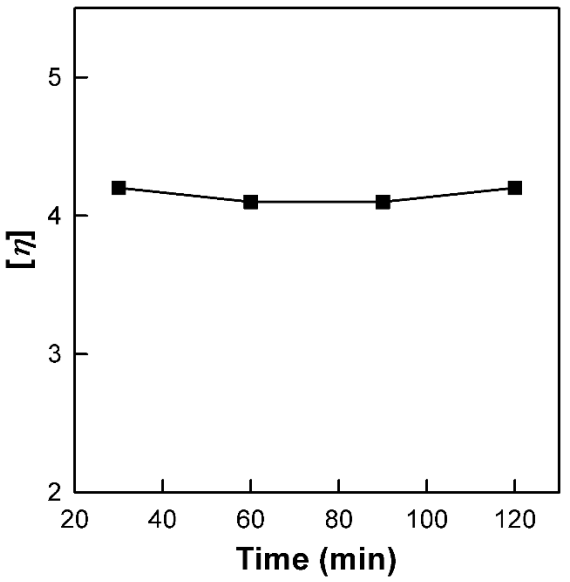



**Figure 3.21** Effect of the polymerization time on I.V(metal salt: 2%, monomer concentration: 4%)

To investigate the effect of acid acceptor, pyridine, 2-picoline and 3-picoline were used during the polymerization and the resulting I.V. values were compared each other. The mole ratio of acid acceptor was fixed with 2.1 equiv of diamines. Because the reaction of amine with acid chloride is nuclephilic reaction, polar aprotic solvent like NMP, DMAc can facilitate the reaction favorably. And organic base like pyridine can form chloroacylium ion as the intermediate with acid chloride and the intermediate can react more easily with amine derivatives than acid chloride. Thus, it was expected that the use of pyridine, 2-picoline and 3-picoline as the acid acceptor results in high molecular weight polymers. But, as shown table 3.3, the effect of acid acceptor on molecular weight was negative. When PPTA is prepared, it has been known that the use of acid acceptor like *N*,*N*′-dimethyl aniline results in high molecular weight polymers. But, in this system, acid acceptors were not suitable for the preparation of high molecular weight polymer. In case of not using the acid acceptors, the highest molecular weight of polymer was obtained. Oh[23] et al reported that when the aromatic polyamides were prepared using pyridine as acid acceptor, the resulting polymers had low molecular weight because the polymerization system became the heterogeneous system by pyridine. The reason is not explained obviously, but also in our system the use of acid acceptor resulted in heterogeneous system, which contribute to the lower molecular weight of polymer, relatively.

The effect of the polymerization time of I.V was investigated also. Fig 3.21 shows the effect of the polymerization time. There was no change in I.V. From this, the reaction of diamine and TPC occurred very fast, which indicated that

the degree of polymerization was determined at the beginning of the polymerization.[23, 28, 29]

**Table 3.3** Effect of acid acceptor on the I.V

| Acid acceptor | [ $\eta$ ] |
|---|---|
| Pyridine | 3.0 |
| 2-Picoline | 2.9 |
| 3-Picoline | 2.9 |
| No use | 9.7 |

Next experiments were carried based on the previous results. We focused on preparation of the anisotropic polymer dope directly after the neutralization, not by re-dissolution of the isolated polymers in NMP + $CaCl_2$. Because lyotropic liquid crystalline behavior is depending on the concentration, only the polymer concentration was variable and other factors were fixed. (metal salt: 2%, low temperature, use of CaO after the solidification of polymer solution). Table 3.4 shows the optical anisotropy and the final dope state of the FAPAB homopolymer after the neutralization with various polymer concentration. At low concentration relatively (below 5%), the optical anisotropy of the polymer solution was not observed. At higher concentration (above 7%), the solutions were optically anisotropic. But, although the neutralizing agent was added, the solidified polymer dopes did not become solution. It was considered because the molecular weight of the polymers were too high. Thus, TPC feed ratio to diamine was reduced from 1 equiv to 0.85 equiv while the polymer concentration was fixed with 10wt%. Table 3.5 shows the results. In polycondensation, the ratio between the monomers

affects largely the final molecular weight of polymer. The more the mole ratio of monomers goes near 1, the more high molecular weight of polymer can be obtained. Thus, it was expected that lower feed ratio of TPC bring lower molecular weight of polymer, which enable to prepare the anisotropic polymer dope. As shown table 3.5, there was a dramatic decrease in I.V when 0.85 equiv of TPC was feeded. But, due to the too low molecular weight, the optical anisotropy disappeared. From this, the polymer dopes with optical anisotropy in the liquid state could not be obtained in FAPAB based homopolymer system. Although hydrogen bonding was interrupted by ester group and fluorine substituent, the polymers were insoluble in organic solvents like NMP, DMAc due to the regularity of polymer backbone.

Thus, non-fluorinated monomer (APAB) was introduced. When the 2 aromatic diamines, FAPAB and APAB are used in the polymerization, the regularity of backbone can be broken, which results in reducing the cohesive energy density of polymers. First, APAB based homopolymer systems were investigated. Table 3.6 shows the change of I.V values in APAB based homopolymer system with the change of TPC feed ratio. It was noticeable that lower molecular weight of polymers relatively were obtained compared to FAPAB based homopolymer system although the same polymerization conditions were applied. This was because the solubility of FAPAB based homopolymer was higher than APAB based homopolymer. When TPC feed ratio was 0.9 equiv, the final dope state of APAB homopolymer was solution while the final dope state of FAPAB homopolymer was high viscous gel (Table 3.5 and 3.6). In case of APAB based homopolymer, when 0.9 equiv of

TPC was added, the polymer dope with optical anisotropy in the liquid state was obtained, not above 0.94 equiv. When the TPC feed ratio was above 0.94 equiv, the optically anisotropic solutions were not obtained due to high molecular weight and the regularity similar to FAPAB based homopolymers. Although the polymer dope with optical anisotropy was obtained (0.9TPC in APAB homopolymer system), its molecular weight was too low. When the polymer dopes having I.V value below 3.0 were spun, the filament was broken very well due to the low molecular weight.

Generally, it has been known that the I.V value of PPTA polymer used in the spinning is 5~6. For any solution spinning process, there are several requirements that the molecular weight of polymer should be as high as possible to maximize the mechanical properties, dope viscosity should be high to aid processability, and polymer concentration should be high to minimize costs because the more solvent is needed in case of spinning at low concentration. In case of APAB homopolymers, the polymer dope soluble in NMP+$CaCl_2$ solution with optical anisotropy were obtained by TPC feed ratio control, but the dope was not suitable for the spinning due to its too low molecular weight. Thus, for the spinning of the polymer dope, the molecular weight of aromatic poly(ester-amide)s should be increased with the maintained solubilities in organic solvents. As above mentioned, preparation of aromatic polyamides suitable for the spinning (optically anisotropic solution with appropriate molecular weight) could not be achieved in FAPAB homopolymer or APAB homopolymer system.

Thus, using FAPAB and APAB, copolymerizations were carried. It was expected that the random distribution of FAPAB and APAB moieties through the backbone brings an increased solubilities in organic solvents. Fig 3.24 shows that the I.V values of poly(ester-amide)s with different feed ratio between FAPAB and APAB. From F 0 to F 100, their I.V values were increased from 6.93 to 9.7. Once FAPAB was used as the monomer, the I.V values of polymers were increased markedly. But, there was no tendency in F25, F50, F75, F100 copolymers. This indicated that the higher solubility of FAPAB moiety help in polymerization. And the loss of both reactivity of functional group and mobility of polymer chain was retarded, which resulted in higher molecular weight of polymers compared to APAB hompolymer.

In copolymerization systems, high molecular weight could be obtained similar to FAPAB or APAB homopolymer systems. Because their I.V values were too high, the molecular weights of copolymers were controlled by TPC feed ratio similar to the homopolymer systems. Because APAB has some advantages in the synthetic route and cost, APAB was used the major part as the monomers in the polymerization as far as possible. In this study, the copolymerizations were focused on F25 copolymer. As shown fig 3.25 and table 3.7, the optically anisotropic solution with appropriate molecular weight of polymer (I.V 5) could be prepared in F25 copolymer. Despite of higher molecular weight than FAPAB or APAB homopolymers, the optically anisotropic polymer solutions were prepared after the neutralization in F25 copolymer. This was because the solubility of copolymer was enahanced by random copolymerization

**Table 3.4** FAPAB based homopolymer with various monomer concentration (wt%)

| Monomer concentration (wt%) | Final dope state | Optical anisotropy | I.V |
|---|---|---|---|
| 17 | Solid and gel | O | 3.0 |
| 13 | Solid and gel | O | 9.7 |
| 9 | High viscous gel | O | 9.0 |
| 6 | Solution | X | 4.5 |
| 4 | Solution | X | 4.0 |

[a] Metal salt: 2%, low temperature (−10℃), CaO was used. The final dope state was determined after the neutralization.

**Table 3.5** Molecular weight control by TPC feed ratio in FAPAB based homopolymer system

| Monomer concentration (wt%) | TPC feed ratio | Final dope state | Optical anisotropy | I.V |
|---|---|---|---|---|
| 13 | 0.85 | Solution | X | 2.0 |
| | 0.9 | High viscous gel | O | 3.6 |
| | 0.95 | Solid and gel | O | 6.5 |
| | 1 | Solid and gel | O | 9.5 |

[a] TPC feed ratio is the ratio of TPC to diamine. metal salt: 2%, low temperature(−10℃), CaO was used.

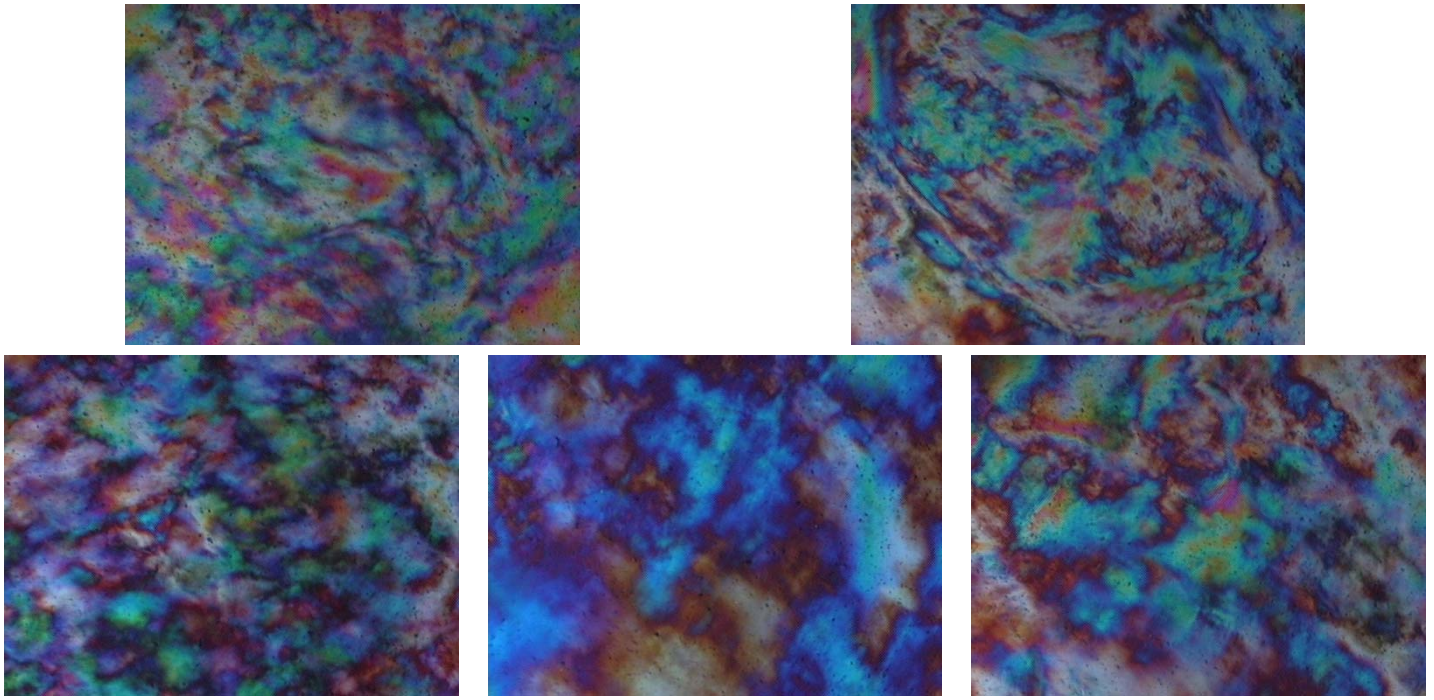


**Fig. 3.22** POM images of FAPAB based homopolymers. (The polymer dopes were sampled in the gel state / concentration: 10wt%)

**Table 3.6** I.V values of APAB based homopolymers with the change of TPC feed ratio

| Monomer concentration (wt%) | TPC feed ratio | Final dope state | Optical anisotropy | I.V |
|---|---|---|---|---|
| 13 | 1 | Solid | O | 6.9 |
| | 0.95 | Gel | O | 4.9 |
| | 0.94 | Gel | O | 4.3 |
| | 0.9 | Solution | O | 3.0 |

[a] Metal salt: 2%, low temperature(−10℃), CaO (equivalent amount to diamines) was used.

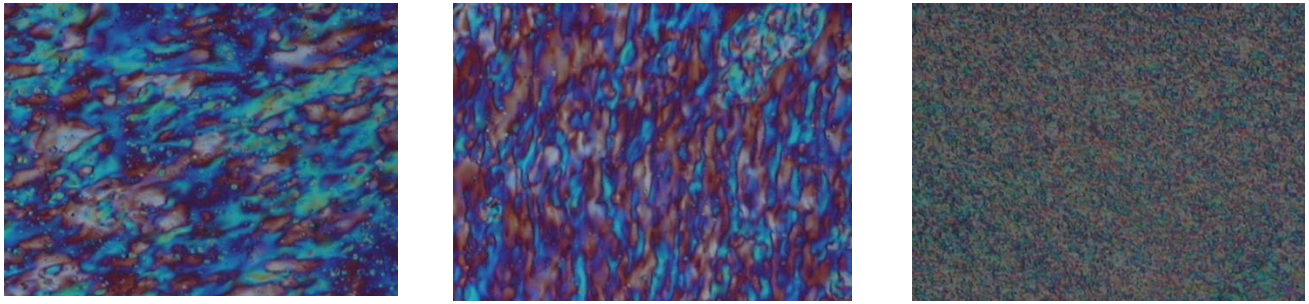


**Fig 3.23** POM images of APAB based homopolymers (at 10wt%)

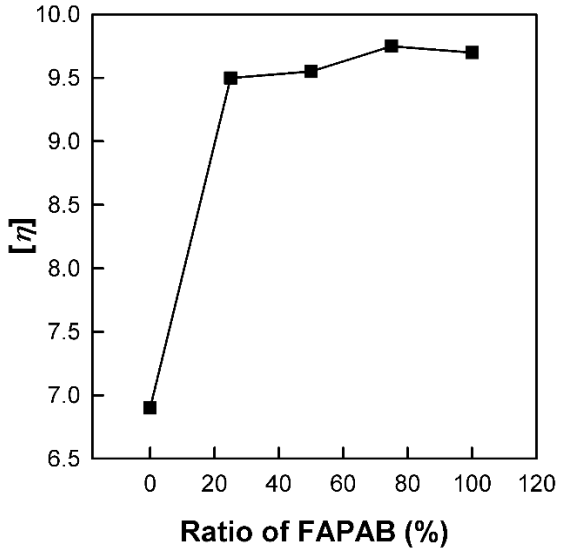



**Fig 3.24** Effect of ratio of FAPAB on the molecular weight of copolymers (Metal salt: 2%, monomer concentration: 13wt%, 1 equiv TPC)

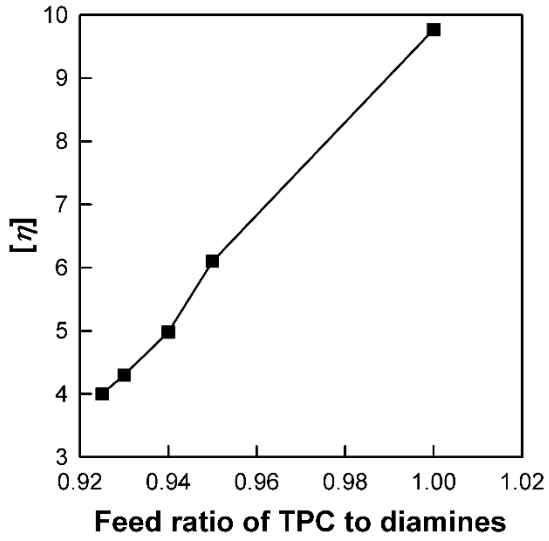



**Fig 3.25** Effect of TPC feed ratio on I.V in copolymer system (FAPAB:APAB=25:75, metal salt: 2%, monomer concentration: 13wt%)

**Table 3.7** I.V values of F 25 copolymers with the different TPC feed ratio

| Monomer concentration(wt%) | TPC feed ratio | Final dope state | Optical anisotropy | I.V |
|---|---|---|---|---|
| 13 | 1 | Solid | O | 9.5 |
| | 0.95 | Gel | | 6.0 |
| | 0.94 | Solution | | 5.0 |
| | 0.93 | Solution | | 4.3 |
| | 0.925 | Solution | | 4.1 |

[a] Metal salt: 2%, CaO (equivalent amount to diamines) was used.

**Table 3.8** Solubilities of obtained aromatic copoly(ester-amide)s in organic solvents.

| Polymer | NMP | DMAc | DMF | NMP + $CaCl_2$ | DMAc + LiCl | THF | $CHCl_3$ |
|---|---|---|---|---|---|---|---|
| F 0 | X | X | X | O | O | X | X |
| F 25 | X | X | X | O O | O O | X | X |
| F 50 | X | X | X | O O | O O | X | X |
| F 75 | X | X | X | O O | O O | X | X |
| F 100 | X | X | X | O O | O O | X | X |

[a] Metal salt: 6%, polymer concentration: 0.5g/dL, temperature: 40℃
[b] OO: soluble, O: soluble by heating for long time, X: insoluble
[c] I.V values – F 0(6.9), F 25,50,75,100(9.5~9.7)

## 3.5 Liquid crystalline behaviors

The liquid crystalline behaviors of the synthesized aromatic poly(ester-amide)s were investigated by POM and Brookfield viscometer. In these experiments, only F 25 copolymer dopes having I.V 5.0 (0.94 equiv TPC) and 4.0 (0.925 equiv TPC) were investigated. Because these polymers are lyotropic liquid crystalline polymer, the formation of liquid crystal is affected by the concentration. Thus, the POM images were obtained at each concentration from low to high concentration. In case of measurement of bulk viscosity of polymer dope, the bulk viscosities were obtained each concentration using Brookfield viscometer. Fig 3.26 shows the change of the bulk viscosity of F 25 copolymer dope depending on the polymer concentration. Under 7wt%, similar to general isotropic polymer solution, the bulk viscosity was increased with the increase of concentration. Especially, at 7wt%, the polymer solution was very viscous gel and its bulk viscosity was highest (27140mPa·s). But, at certain concentration (critical concentration) (8wt%), the optical anisotropy appeared and the viscosity was decreased rapidly up to 11wt% (6640 mPa·s). This is a characteristic of optical anisotropic solution. Under the critical concentration, the rod-like polymer chain is randomly distributed in the solution. But, above the critical concentration, the random rods starts to align parallel to each other in given space, which results in the formation of liquid crystal. Because the slippage of the liquid crystal domain occurred more easily under liquid crystalline state, the domains flow more easily to the direction of shear force, which brought

the decrease in the bulk viscosity. It was noticeable that high molecular weight and low molecular weight F 25 copolymers exhibited different behaviors in the decrease of the bulk viscosity. In lower molecular weight polymer, the critical concentration was shifted to higher concentration and the numerical value of the bulk viscosity was lower than high molecular weight polymer. There was a dramatic decrease in the bulk viscosity in high molecular weight polymer. It was considered that in low molecular weight, the higher concentration was required to align parallel to each other. This results corresponded the previous work[45,48]. Compared to APAB based homopolymer, although F 25 copolymer had higher molecular weight, F 25 copolymer could form the optically anisotropic solution due to high solubility. Fig 3.27 shows the POM images of F 25 polymer dope having I.V 5.0 at each concentration. Under 6wt%, no liquid crystal was observed, but the liquid crystal started to form at 7wt% gradually. The texture resulting from the formation of liquid crystal was observed from 8wt%. Thus, the critical concentration of F 25 copolymer was confirmed around 8wt% from the results of bulk viscosity and POM.

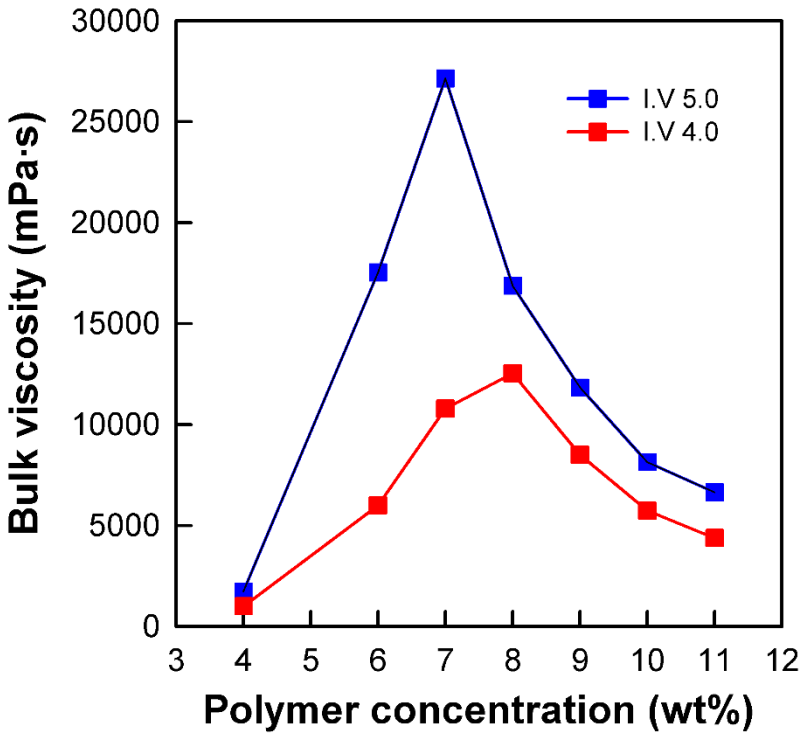



**Figure 3.26** Bulk viscosity of F 25 copolymer dope

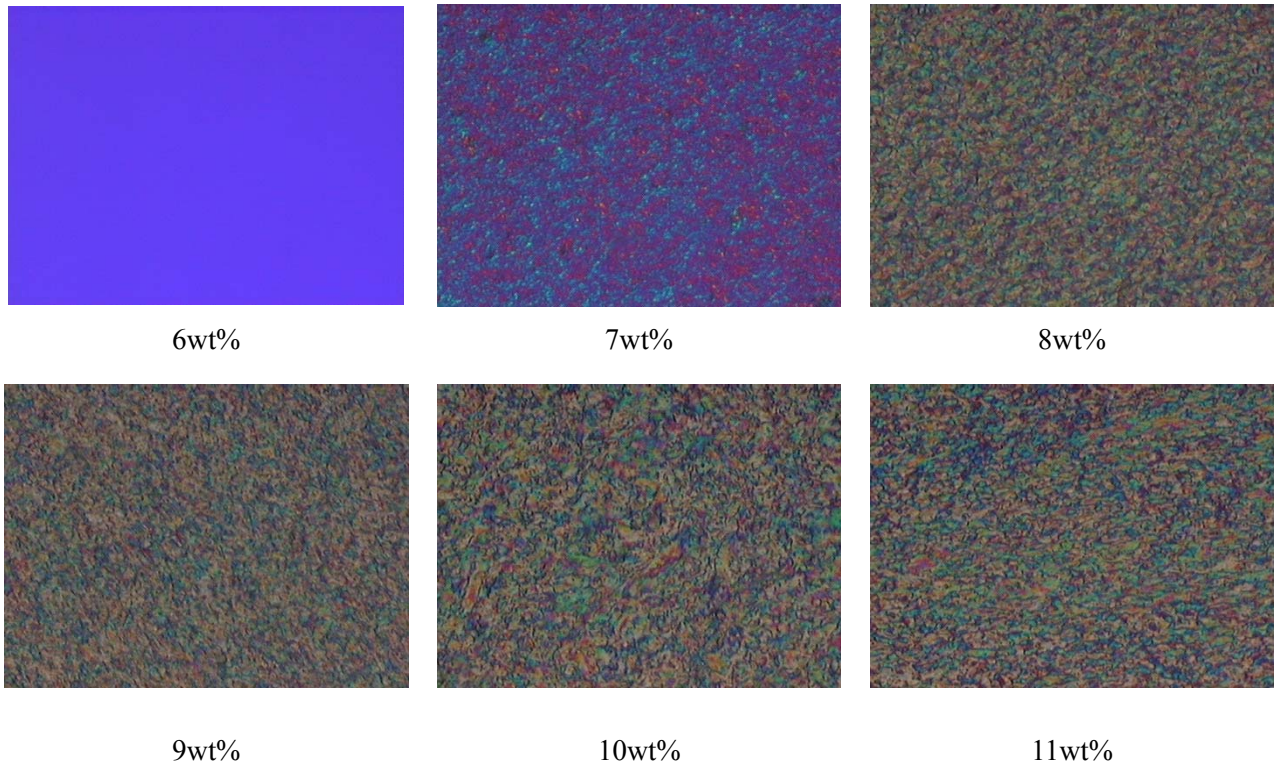



**Fig 3.27** POM images of F 25 copolymer dope

# Chapter 4. Conclusions

In this study, 2 aromatic diamines FAPAB and APAB having an ester group were designed and synthesized. The wholly aromatic poly(ester-amide)s from the synthesized aromatic diamines exhibited good thermal stability and crystallinity similar to PPTA. In FAPAB and APAB homopolymer systems, the corresponding poly(ester-amide)s exhibited liquid crystal formation respectively, but it was hard to obtain the anisotropic polymer dope with appropriate molecular weight due to their low solubility in organic solvents resulting from their regularity. To break the regularity and enhance the solubility of polymer in organic solvents, random copolymerizations were carried using FAPAB and APAB as monomers with different mole ratio. As the results, the solubility of copoly(ester-amide)s was quite increased. Especially, under the condition of monomer concentration 13wt%, metal salt 2%, 0.94 equiv of TPC feed ratio and the diamine composition FAPAB 25%, APAB 75%, moderate high molecular weight (I.V 5.0) of poly(ester-amide)s could be obtained and the optically anisotropic polymer solution was prepared from the condition in NMP + $CaCl_2$. Its bulk viscosity was increased up to 7wt% and decreased from 8wt% to 11wt% rapidly due to the formation of liquid crystal. This was proved by POM also. From 8wt%, the texture resulting from the formation of liquid crystal was observed. As this is a major characteristic of lyotropic behavior, the poly(ester-amide)s exhibited lyotropic behavior in organic solvent.

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# 초 록

본 연구에서는 기존의 방향족 폴리아마이드의 강한 수소결합을 줄이기 위하여 에스터 그룹을 갖는 2개의 방향족디아민, FAPAB와 APAB를 설계 및 합성하였다. 2개의 방향족 디아민, FAPAB 및 APAB의 단일중합 시스템에서 고분자량의 고분자를 얻을 수 있었으며 합성된 고분자는 좋은 열적특성 및 기존 PPTA와 유사한 결정성을 보였다. 또한, 8wt% 이상의 농도에서 액정을 형성함을 보였다. 그러나 단일중합 시스템만으로는 에스터 그룹에 의해 수소결합밀도가 감소하더라도 어느 정도의 규칙성을 가지므로 유기용매에 대한 용해성이 좋지 않아 중화제를 투입하여도 I.V 4.5 이상의 분자량을 갖는 이방성 고분자 용액이 제조되지 못하였다. 이를 해결하기 위하여 2개의 방향족 디아민단량체의 공중합을 실시하여 그 규칙성을 깨뜨림으로써 공중합 폴리에스터-아마이드 고분자의 유기용매에 대한 용해성을 향상시키고자 하였다. 그 결과, FAPAB 기반 고분자의 APAB 기반 고분자보다 더 높은 용해성으로 인하여 APAB 단일중합체보다 모든 중합조건에서 더 고분자량의 고분자를 얻을 수 있었으며 특히, 단량체 농도 13wt%, 금속 염 2%, TPC 투입비율 0.94, FAPAB와 APAB의 비율이 25:75 일 때 I.V 5의 이방성 고분자 용액이 NMP + $CaCl_2$ 시스템에서 만들어졌다. FAPAB, APAB 기반 각각의 단일중합의 경우에는 I.V 5에 가까운 이방성용액 제조가 불가능하였으므로 이는 random 공중합에 의해 효과적으로 고분자의 용해성이 향상되었음을 의미한다. 제조된 이방성용액의 용액점도를 Brookfield 점도계로 측정한 결과, 7wt%에서 최고 점도값을 보였으며 8wt%부터는 서서히 감소하여 11wt%에서 최저 점도값을 보였다. 이는 편광현미경에서도 확인할 수 있으며 8wt%부터 액정형성에 의한 texture가 나타났다. 고농도에서 오히려 점도가 감소하는 이러한 현상은 유방성 액정고분자의 특이한 현상으로서 본 연구에서 합성된 공중합 폴리에스터-아마이드 역시 유기용매인 NMP에서 유방성 액정거동을 보임을 확인하였다.

주요어: 아라미드, 액정, 유방성, 방향족 폴리아마이드, 용해성, 유기용매, 수소결합

학 번: 2012-23930