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공학석사 학위논문

**Synthesis and Characterization of  
Chemically Modified Aromatic  
Poly(ester-amide)s Exhibiting Liquid  
Crystalline Properties in Organic  
Solvents**

유기용매에서 액정 특성을 나타내는 화학적으로  
변형된 방향족 폴리아미드/에스테르의 합성과 특성

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서울대학교 대학원

재료공학부

서준식

**Abstract**

**Synthesis and Characterization of  
Chemically Modified Aromatic  
Poly(ester-amide)s Exhibiting Liquid  
Crystalline Properties in Organic  
Solvent**

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Aromatic polyamides are researched during decades to make good use of their excellent thermal and mechanical properties. However, due to their poor solubility in common organic solvents resulting from the strong inter-chain hydrogen bonding, aromatic polyamides are difficult to process and apply to practical usage. Therefore, we synthesized novel chemically modified aromatic poly(ester-amide)s to overcome the weakness. In order to reduce the hydrogen bonding level, ester group was introduced between two aromatic rings and chlorine group is also included on the one of rings to enhance the solubility and diminish the level of inter-chain hydrogen bonding. To make the anisotropic solution dope, two kinds of diamines were used for polymerization which led to break the regularity of repeating groups and increase solubility to the organic solvent. As a result, the polymer solution which have the critical concentration at 6wt% was could be made.

**Keywords: Aramids, Aromatic Polyamides, Solubility, Organic solvents,  
Liquid crystalline, Lyotropy**

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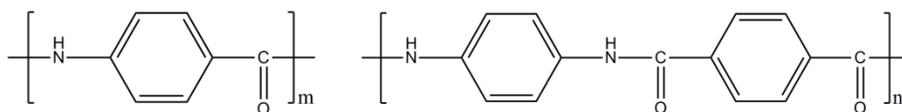
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## Chapter 1. Introduction

Aromatic polyamides abbreviated to aramids are high-performance polymers which give modern fiber industries useful properties like tenacity, thermal stability and good resistance to abrasion and chemical substances.<sup>1-5</sup> By these characteristics, aromatic polyamides have been used as various materials for aerospace, munitions industry, protection equipments and sports. They have mainly commercialized in the shape of fiber and also been researched through decades to enhance the strength of it.<sup>6-16</sup>

To synthesize these polymers, two functional group, amine and acid chloride, have to react in the homogeneous system. By using this polymerization method, poly(*p*-benzamide) (PBA)<sup>17-19</sup> and poly(*p*-phenylene terephthalamide) (PPTA)<sup>19,20</sup> were primordially synthesized. The former was successfully polymerized and suggested the possibility to be made in the form of fiber. However, a monomer used in the polymerization, *p*-aminobenzoyl chloride, was hard to be synthesized and stored for long periods because of high reactivity of it. Therefore, the latter began to receive attention as the source of high-performance fiber. In the case of PPTA, two monomers, *p*-phenylene diamine and terephthaloyl chloride, was used for polymerization. In contrast with the monomer of PBA, two monomers of PPTA was easy to be



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

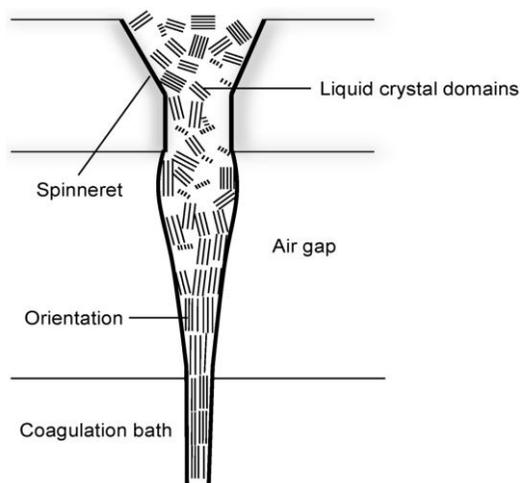
synthesized and stored for a long time.

The first product of aromatic polyamide fiber was commercialized by Du Pont in the name of 'Kevlar'.<sup>21</sup> It is an excellent example of the innovation process where a laboratory discovery is placed into commercial production. The corporation not only manufactured the fiber which exhibited great mechanical and thermal properties but also increased productivity by adopting a series of air gap spinning process.<sup>22-24</sup> This process enabled polymer solution to be wound in the form of fiber as soon as it was precipitated in the water. As the polymer pass through the water, salts and water-soluble solvent was eliminated from it.

While the polymer solution injected from outlet, each polymer chains are forced to align parallel between particular polymer concentration in the solution.<sup>25-28</sup> This phenomenon which is called lyotropy, or exhibition of liquid crystalline properties in the solvents. The liquid crystal is a material which has characteristics between liquid and solid state and also exhibits an anisotropic property that makes the material to be seen opaque liquid. As to polymers, liquid crystalline properties are often observed from polymer solutions where polymer chains have rod-like conformation. Because of their rigid structure, polymer chains are hard to be entangled each other, but rather easy to flow in the same direction. In this condition, the polymer solution shows nematic state where each chain has no regularity of position, but one of direction.

Meanwhile, the lyotropy is important component in the spinning system because it enables an aramid fiber to obtain higher strength and stiffness than

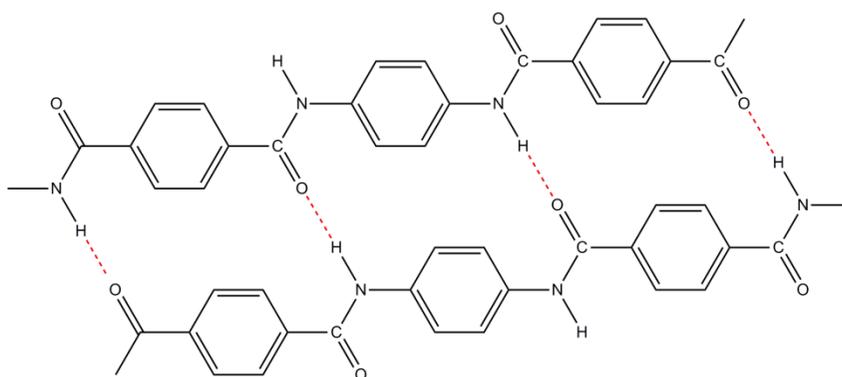
a fiber produced from isotropic polymer solutions. When the anisotropic polymer solution flows through the fine tube, as it is mentioned earlier, polymer chains are aligned in the same direction. After that, the solution is precipitated in the water and chains are stiffened in the shape of parallel structure. This is the reason why the fiber manufactured from lyotropic polymer solution has excellent mechanical properties. Therefore, liquid crystalline properties have to be maintained stably by optimizing polymerization condition.



**Fig 1.2** Schematic diagram of air gap spinning process

Fibers obtained from nematic solution of aramids are at present employed in a variety of applications where high mechanical strength and thermal resistance are required. However, extremely limited solubility of them restricted preparation and characterization of high-molecular weight products as well as their processing from solution. These properties of the aramids are

due to the inter-chain hydrogen bonding generated between each amide group.<sup>29,30</sup> Because of their high cohesive energy resulting from hydrogen bonding between polymer backbones, most solvents cannot dissolve aramids (PPTA) excluding sulfuric acid. Concentrated sulfuric acid is strong enough to break the hydrogen bonding and decouple polymer chains and, for that reason, it is used in spinning systems to produce aramid fibers. Unfortunately, usage of it causes corrosion of process facilities and exerts a bad influence on environment. Therefore, it is important to synthesize novel aramids which can dissolve in common organic solvents.



**Fig 1.3** Inter-chain hydrogen bonding of PPTA

Aromatic polyamides have been modified chemically with a variety of methods to improve solubility. One of the methods was to introduce some flexible segments like aliphatic domains on the polymer backbone.<sup>31,32</sup> In this case, enhancement of solubility was successful, but it was hard to observe lyotropic properties from polymer solutions due to decrease of chain rigidity.

The other strategy like introducing monomers causing a parallel displacement also exhibited great solubility to organic solvents even though it was unsuccessful to reveal anisotropy because kinked structure interrupts slip of polymer chains.<sup>33,34</sup>

There were other attempts to reduce the effect of inter-chain hydrogen bonding by replacing an amide hydrogen with an alkyl or aryl group.<sup>35,36</sup> This was a very effective technique for increasing solubility of aromatic polyamides in organic solvents. That is because *N*-substitution interrupts the fraction of amide bonds having a planar *trans*-conformation. However, as we see above, decrease of chain rigidity cannot lead to exhibition of liquid crystalline behavior just the same case with *N*-substituted polymers. There is a trade-off relationship between solubility and liquid crystalline behavior. Thus, it has to be considered that the solubility of aromatic polyamides should be improved while their chain conformation is not affected.

Through efforts of many researchers, it is revealed that the best way to maintain both liquid crystalline properties and excellent solubility to organic solvents is introducing various functional groups to benzene rings. T. I. Bair, P. W. Morgan and F. L. Killian reported that chlorinated PPTA (Cl-PPTA) was soluble in the organic solvent and the polymer solution exhibited lyotropic behavior.<sup>37</sup> Meanwhile, T. J. Oh et al reported that cyanated PPTA (CN-PPTA) was entirely soluble in some organic solvents containing alkali metal salt while the polymer solution exhibited stable liquid crystalline behavior.<sup>38</sup> They also announced that CN-PPTA solution could be spun to fibers with high tensile strength and modulus.<sup>39</sup> Another group of W. R. Krigbaum et al

synthesized aromatic polyamides including phenyl pendant group as a substituent on the benzene ring.<sup>40</sup> These polymers not only exhibited lyotropic behavior in the organic solvent but also had high intrinsic viscosity which is necessary for excellent mechanical properties of fibers. Besides mentioned examples, R. S. Irwin reported novel lyotropic aramid consisting of a biphenyl moiety with trifluoromethyl substituent group.<sup>41</sup> Generally, aromatic polyamides comprised of biphenyl moieties which have diverse substituent do not exhibit liquid crystalline properties because the conformation of moieties is too twisted to maintain rigid rod-like structure. However, Irwin proved it could be made to anisotropic solution by adding some kind of metal salt while keeping specific range of salt concentration. Once cations from metal salt were located between a fluorine atom of an electronegative  $\text{CF}_3$  group and an oxygen atom of an adjacent carbonyl, an electrostatic bridge was formed to enable the planar structure of biphenyl moieties. Induction of lyotropy in aramid solutions by ionic species has not previously been reported, so it is of great significance in this field. Using the strategies as noted above, much endeavor has been made to create structurally modified aramids having better solubility and processability while it possess their superior thermal and mechanical properties.

In this study, greenly designed diamine monomer containing an ester group between two benzene rings and a chlorine group on one of benzene rings was synthesized. The ester group was introduced to reduce the hydrogen bonding which is generated between amide bonds. In the case of chlorine group, two main reasons were considered to be introduced as a substituent group. First, it

helps polymers to dissolve in the organic solvent. The chlorine group has certain electro-negativity so that it can interact with salt ions, especially cations, which interact with amide groups of the organic solvent like *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone. Second, the chlorine group helps to diminish the level of inter-chain hydrogen bonding. Because the atom size of it is bulky, it can increase the length of the hydrogen bonding to make it weaken. So, for these reasons, the diamine monomer synthesized and polymerized to make novel aromatic polyamide. And the polymer also analyzed to investigate their solubility, thermal properties and liquid crystalline behavior.

## Chapter 2. Experimental Section

### 2.1 Materials

Various reagents were purchased from Sigma-Aldrich, Alfa-Aesar, TCI chemicals and Samchun chemicals which used as they are received to the lab or stored in the dry place. *N,N*-Dimethylacetamide (DMAc) (Samchun chemicals), *N*-Methyl-2-pyrrolidone(NMP) (Samchun chemicals), 4-nitrophenol (Alfa Aesar), 4-nitrobenzoyl chloride (Alfa Aesar) and 2-Chloro-4-nitrophenol (TCI chemicals) were used without any further purification. Calcium chloride (Sigma-Aldrich) was dried under vacuum at 120 °C before usage.

### 2.2 Synthesis and polymerization

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

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 in a two-neck round bottom flask at 70 °C. To the solution, 66.7 g (0.36 mol) of 4-nitrobenzoyl chloride was added in several portions. The solution was stirred at 70 °C for additional one hour. After that, the solution was poured into 600 ml water and a white precipitate appeared. The precipitate was collected by suction filtration and washed thoroughly with water two times. 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. Finally, the product was dried under vacuum at 40 °C for more than 8 hours to give compound of 90 g as white powder. (87% in yield)

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44 (d, 2H), 8.34-8.39 (m, 6H)

Anal. calcd for  $\text{C}_{13}\text{H}_8\text{N}_2\text{O}_6$  ( $M_w=288.04$ ): C, 54.18; H, 2.80; N, 9.72; O, 33.31%. Found: C, 54.01; H, 2.87; N, 9.67; O, 33.45%.

IR (KBr):  $3100\text{ cm}^{-1}$  (aromatic ring str.),  $1750\text{ cm}^{-1}$  (C=O str.),  $1550$ ,  $1480$ ,  $1350\text{ cm}^{-1}$  ( $\text{NO}_2$  str.) and  $480\text{ cm}^{-1}$  ( $\text{NO}_2$  roc.)

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

In this study, a stannous chloride (II) ( $\text{SnCl}_2$ ) was used as a reducing agent of nitro groups. The stannous chloride (II) has been a basic reductant for long periods because of its strong reducing power and selectivity for nitro groups.<sup>42,43</sup> A two-neck round bottom flask connected with a gas cock was charged with compound NPNB (40.0 g, 0.139 mol) and stannous chloride (II) (211 g, 1.11 mol) at room temperature. 300 mL of 95% ethanol and 10 ml of concentrated hydrochloric acid were added and the reaction mixture was heated to reflux at 70 °C. As the reaction progressed, the mixture became homogeneous solution. At that time, much heat of reaction generated and the solvent boiled vigorously. (The reaction must be progressed in the open system to prevent rupture of the septum of an outlet). After one hour, the solution was basified with saturated  $\text{K}_2\text{CO}_3$  solution until the pH of solution became 9~10. After the adjustment of pH, the suspension was extracted with

ethyl acetate 3 times. The organic layer was washed with water, brine and dried magnesium sulfate. Then ethyl acetate was evaporated and the crude product was recrystallized in ethanol to give compound 23.7 g as yellowish white needle-like crystal. (75 % in yield)

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  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  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$  ( $M_w=228.25$ ): C, 68.41; H, 5.30; N, 12.27; O, 14.02%. Found: C, 68.20; H, 5.39; N, 12.19; O, 14.22%.

IR (KBr): 3400 and 3320  $\text{cm}^{-1}$  ( $\text{NH}_2$  str.), 3070  $\text{cm}^{-1}$  (aromatic ring str.), 1700  $\text{cm}^{-1}$  (C=O str.) and 1590  $\text{cm}^{-1}$  ( $\text{NH}_2$  ben.)

### 2.2.3 Synthesis of 2-Chloro-4-nitrophenyl-4'-nitrobenzoate (CNPNB)

2-Chloro-4-nitrophenyl-4-nitrobenzoate (CNPNB) was also prepared similarly with the synthetic process of 4-nitrophenyl-4-nitrobenzoate (NPNB). A solution of 50 g (0.29 mol) of 2-Chloro-4-nitrophenol in 300 ml DMAc was stirred in a 2-neck round bottom flask at room temperature. Next, to the solution, 4-nitrobenzoyl chloride 57.5 g (0.31 mol) was added in several portions. And then, the solution mixture kept on stirring 24 hours. In case of having bulky chlorine atom near the reacting functional group, It is necessary to maintain stirring as long as possible to increase the yield of product. As the reaction was progress, the mixture began to be opaque gradually. After 24 hour, the solution was poured into 700 ml water and a greenish white precipitate appeared. The precipitate was collected by suction

filtration and washed thoroughly with water two times. Finally, the filter cake was washed with acetone and collected by suction filtration. Finally, the product was dried under vacuum at 40 °C for more than 8 hours to give compound of 92.7 g as greenish white solid. (79% in yield)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ -*d*):  $\delta$  7.91 (d, 1H), 8.35-8.48 (m, 5H), 8.56 (d, 1H)

Anal. calcd for  $\text{C}_{13}\text{H}_7\text{FN}_2\text{O}_6$  ( $M_w=322.66$ ): C, 48.39; H, 2.19; N, 8.68; O, 29.75; Cl, 10.99%. Found: C, 48.32; H, 2.22; N, 8.64; O, 29.86; Cl, 10.96%.

IR (KBr): 3100  $\text{cm}^{-1}$  (aromatic ring str.), 1750  $\text{cm}^{-1}$  (C=O str.), 1490  $\text{cm}^{-1}$  ( $\text{NO}_2$  antisym str.), 1345  $\text{cm}^{-1}$  ( $\text{NO}_2$  sym str.), 750  $\text{cm}^{-1}$  (C-Cl str.)

#### **2.2.4 Synthesis of 2-Chloro-4-aminophenyl-4'-aminobenzoate (CAPAB)**

Likewise with the synthetic progress of APAB, a two-neck round bottom flask was charged with compound CNPNB (40.0 g, 0.124 mol) and stannous chloride (II) (188 g, 0.992 mol) at room temperature. 300 mL of 95% ethanol and 10 ml of concentrated hydrochloric acid were added and the reaction mixture was heated to reflux at 70 °C. As the reaction progressed, the mixture became homogeneous solution. At that time, much heat of reaction generated and the solvent boiled vigorously. (This reaction also has to be progressed in the open system to prevent rupture of the septum of an outlet). After one hour, the solution was basified with saturated  $\text{K}_2\text{CO}_3$  solution until the pH of solution became 9~10. After the adjustment of pH, the suspension was extracted with ethyl acetate 3 times. The organic layer was washed with water, brine and dried magnesium sulfate. Then ethyl acetate was evaporated and the

crude product was recrystallized in ethanol to give compound 23.8 g as white tetragonal board-like crystal. (73 % in yield)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3-d$ )  $\delta$  5.31 (br s, 2H), 6.14 (br s, 2H), 6.52 (dd, 1H), 6.62 (d, 2H), 6.68 (d, 1H), 6.93 (d, 1H), 7.76 (d, 2H)

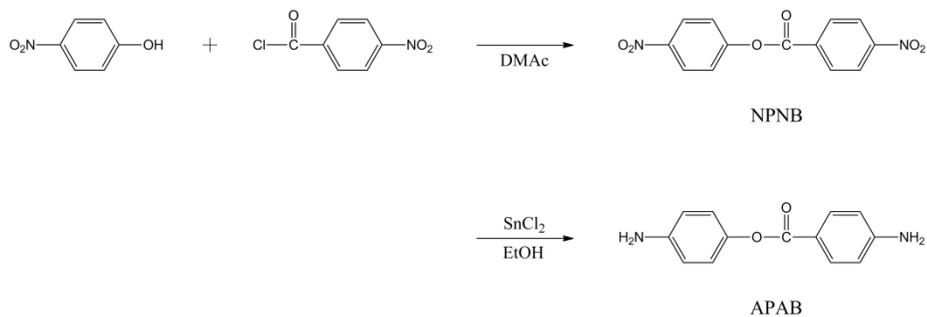
Anal. calcd for  $\text{C}_{13}\text{H}_{11}\text{FN}_2\text{O}_2$  ( $M_w=262.69$ ): C, 59.44; H, 4.22; N, 10.66; O, 12.18; Cl, 13.50%. Found: C, 59.39; H, 4.27; N, 10.61; O, 12.28; Cl, 13.45%.

IR (KBr): 3400 and 3320  $\text{cm}^{-1}$  ( $\text{NH}_2$  str.), 1720  $\text{cm}^{-1}$  (C=O str.), 1590  $\text{cm}^{-1}$  ( $\text{NH}_2$  ben.), 770  $\text{cm}^{-1}$  (C-Cl str.)

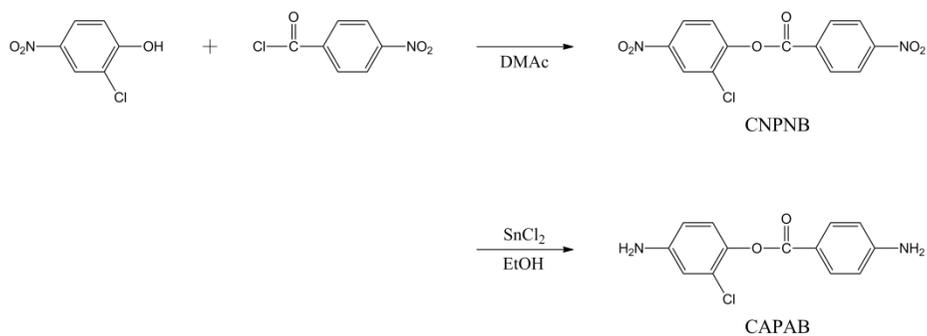
## 2.2.5 Polymerization of monomers

Aromatic polyamide was prepared by low-temperature polycondensation between the synthesized aromatic diamines and terephthaloyl chloride (TPC). Scheme 2.3 shows the polymerization route of it. *N*-methyl-2-pyrrolidone (NMP) and calcium chloride ( $\text{CaCl}_2$ ) was selected as a polymerization solvent and metal salt respectively. Calcium oxide ( $\text{CaO}$ ) was used as the neutralizing agent to neutralize hydrogen chloride generated during the polymerization. The stirring rate was fixed at 250 rpm. The preparation was described as the general procedure. To a 500 mL, 3-necked round bottom flask equipped with a mechanical stirrer and a cock connected with argon gas tube, NMP 50.3 g (monomer concentration 10 wt%) was added and  $\text{CaCl}_2$  0.9784 g (Ratio: 2 g of  $\text{CaCl}_2$  per 100ml of NMP) was dissolved in NMP. After the dissolution of  $\text{CaCl}_2$ , aromatic diamine CAPAB 1 g (0.00381 mol) and APAB 2.6 g (0.0114 mol) (Ratio was 25:75) was added and dissolved. When the aromatic diamine was fully dissolved in NMP +  $\text{CaCl}_2$  system, the flask was placed in ice bath

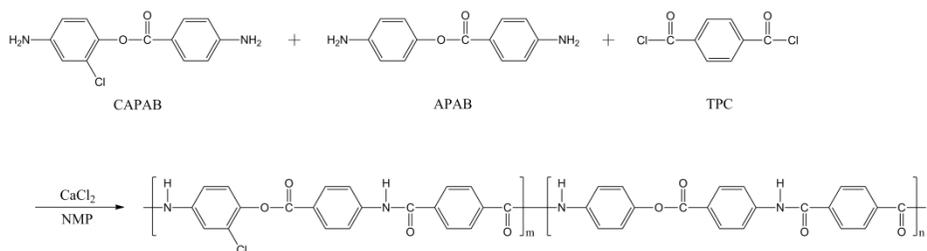
to lower the temperature of the solution less than 5 °C. After 10 minutes, TPC 3.09 g (0.0152 mol) was added in one portion and the reaction mixture was stirred vigorously at 250 rpm. After a few minutes, the reaction mixture became gel, solution, or solid depending on the polymerization condition. In case of not using the neutralizing agent, to collect the polymer from the solvent for analysis, 500 ml DI water was poured into the reaction flask, then the synthesized polymer was precipitated. The precipitated polymer was collected by suction filtration. The filtrate was pulverized by mixer and washed with hot water two times to extract solvent, metal salt and hydrogen chloride. Finally, obtained polymer precipitate was washed with acetone thoroughly to eliminate unreacted monomer, collected by suction filtration and dried under vacuum at 100 °C for 24 hrs. In case of neutralizing the polymer dopes, the neutralizing agent, CaO 0.897 g (equimolar amount to diamines) was added. The mixture was well-mixed to make the neutralizing agent percholate into the solidified polymer solution and wait about 24 hours for it to dissolve. Normally, the reaction mixture became solution, but sometimes solid or gel after the neutralization depending on the polymerization condition.



**Scheme 2.1** Synthetic route of 4-aminophenyl-4'-aminobenzoate (APAB)



**Scheme 2.2** Synthetic route of 2-Chloro-4-aminophenyl-4'-aminobenzoate (CAPAB)



**Scheme 2.3** Copolymerization scheme of CAPAB and APAB

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

Polymer name	Feed ratio (%)	
	CAPAB	APAB
Cl 100	100	0
Cl 75	75	25
Cl 50	50	50
Cl 25	25	75
Cl 0	0	100

## **2.3 Characterization**

### **2.3.1 Analysis of chemical structures**

Chemical structures of monomers handled in this study were identified by  $^1\text{H}$  NMR (Avance DPX-300). The identification of functional groups was carried with FT-IR (Thermo Scientific, Nicolet 6700). The spectra of samples were obtained by being made to pellets using potassium bromide. Vibrational transition frequencies are exhibited in wavenumbers ( $\text{cm}^{-1}$ ). Elemental analyses were conducted with Flash1112, Flash2000 model and quantified with TCD detector in dynamic flash combustion method.

### **2.3.2 Computer simulation of geometries**

Optimized geometries of monomers and polymers were obtained by density functional theory calculation method based on B3LYP function and 6-31G basis set. In case of polymers, the repeating unit including aromatic diamine and terephthalamide was optimized instead of whole polymer structure.

### **2.3.3 Thermal analysis**

Thermogravimetric analyses were carried out with TGA 2050 Thermogravimetric Analyzer model (TA instrument) at a heating rate of  $10^\circ\text{C}/\text{min}$  under flow of nitrogen gas. Thermal transition temperatures were determined by DSC 2920 differential scanning calorimeter (TA instrument). In the DSC analysis, the heating and cooling rate were fixed with  $10^\circ\text{C}/\text{min}$ .

### **2.3.4 Observation of anisotropic behavior**

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 the room temperature. The optical anisotropy was observed by POM after the polymer solution was coated on the slide glass.

### **2.3.5 Measurement of viscosities**

Molecular weights of synthesized polymers were determined from intrinsic viscosity. Polymers dried in the 100°C vacuum oven was dissolved in NMP at the polymer concentration of 0.5 g/dL. Calcium chloride as a metal salt was dissolved in all solutions at the concentration of 2% to increase the solubility of polymers to solvent. This measurement was progressed with Cannon-Fenske viscometer at 30°C and the temperature maintained by the circulating system of the water bath.

## Chapter 3. Results and Discussion

### 3.1 Synthesis and Characterization

After the synthesis of monomer, chemical structures of 4-nitrophenyl-4'-aminobenzoate (NPNB), 4-aminophenyl-4'-aminobenzoate (APAB), 2-Chloro-4-nitrophenyl-4'-nitrobenzoate (CNPNB), 2-Chloro-4-aminophenyl-4'-aminobenzoate (CAPAB) are identified by  $^1\text{H}$  NMR, as shown in Figure 3.1-4.

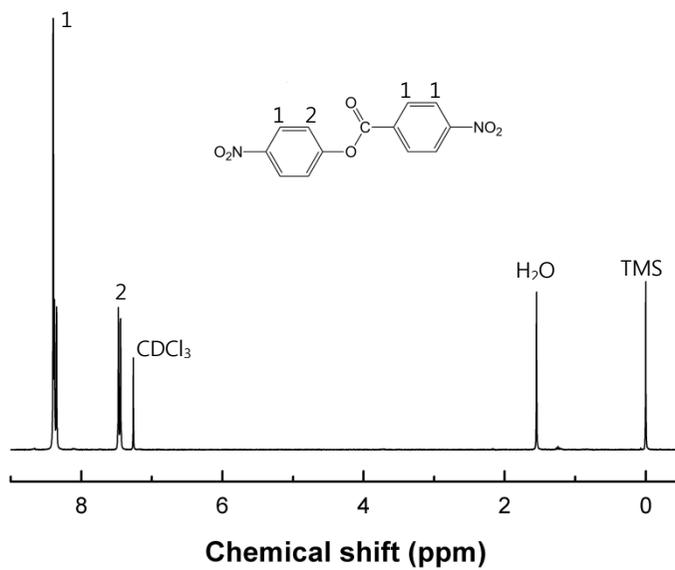
In the case of synthesizing NPNB and CNPNB, it was better to use tetrahydrofuran, as an aprotic solvent, and pyridine, as an acceptor of generated hydrogen chloride, when the reaction scale is small because these solvents are suitable for extraction. However, as capacity of the reaction is scaled up, it is hard to treat all products with several extractions. Therefore, in regard of electrophilic substitution reaction like this, it is better to use the polar aprotic solvent like *N,N*-dimethylacetamide which promotes the reaction with its excellent polarity. When this solvent is used, reacted solution is just needed to pour in the water and filter the precipitate. Of course, there are many impurities because there is no process of recrystallization, but they are separated in the next step. Especially, it is convenient to obey this method during the synthesis of NPNB. That is because the recrystallized product of it has so large volume that it is difficult to obtain it from large scale reaction.

In conclusion,  $^1\text{H}$  NMR and elemental analysis data show that all procedures of each product are properly progressed. In case of synthesizing

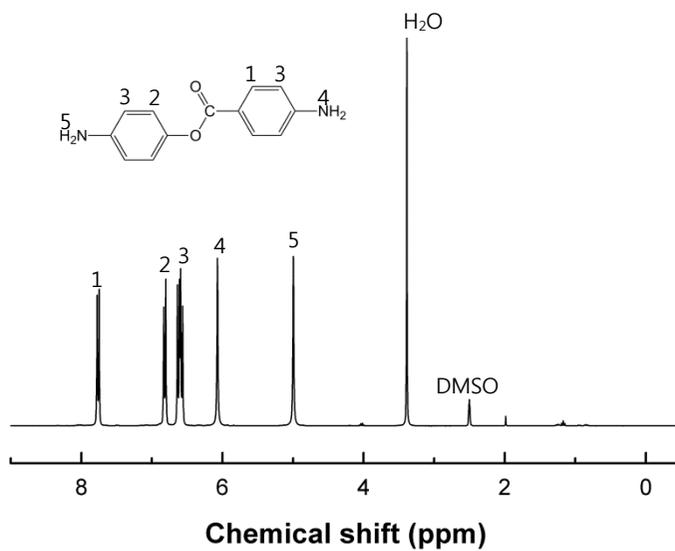
APAB and CAPAB, it was confirmed that  $\text{SnCl}_2$  was the best reducing agent which has the selectivity to nitro groups. In  $^1\text{H}$  NMR data, all peaks of each product were distinct and there was no any peak of impurity apart from the solvent. From these results, it is assured that recrystallization is the effective way to eliminate impurities.

In table 3.1, there are elemental analyses results of NPNB, APAB, CNPNB and CAPAB showing that the calculated values of content of C, H, N, O, Cl 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 result, highly pure diamines were synthesized properly.

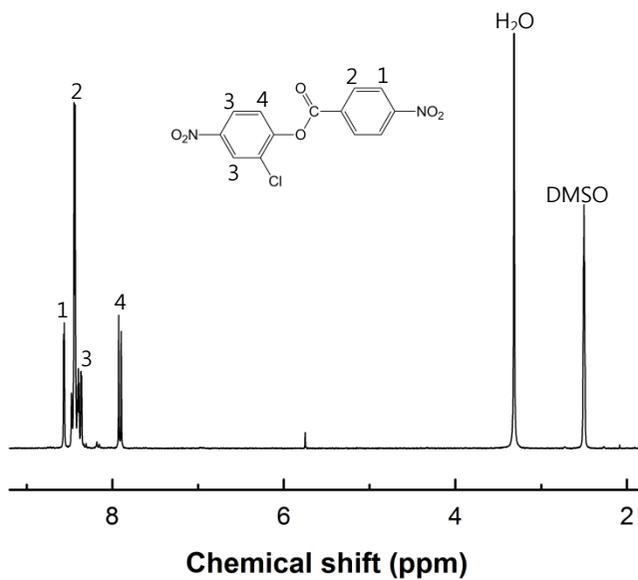
With these diamines, aromatic poly(ester-amide)s were successfully synthesized. The intrinsic viscosities of the polymers are higher than 8 except for APAB based homopolymers. Considering that the normal I.V. values of PPTA is 4~5, high molecular weight of aromatic poly(ester-amide)s could be obtained. The functional groups of aromatic poly(ester-amide)s were identified by FT-IR in fig 3.7.



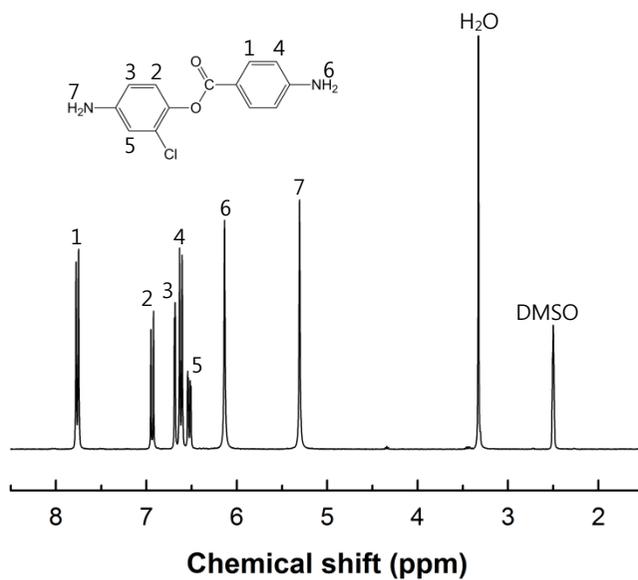
**Figure 3.1** Chemical structure and  $^1\text{H}$  NMR spectrum of NPNB



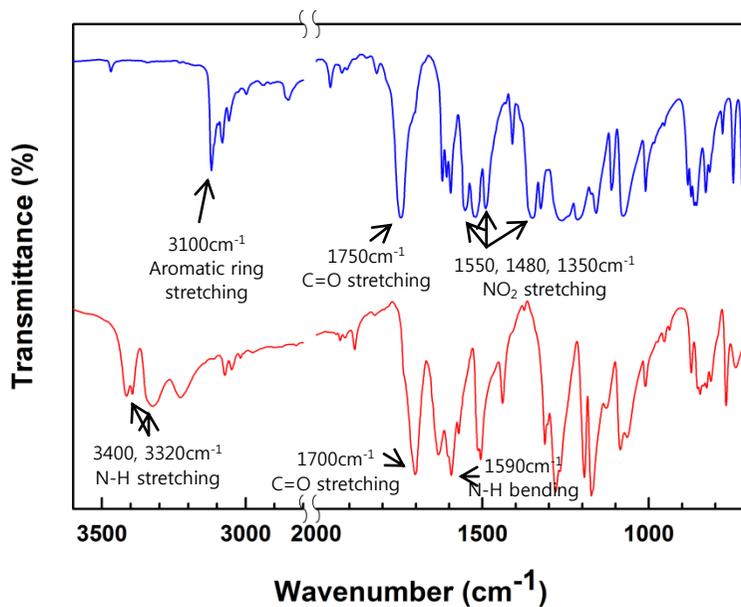
**Figure 3.2** Chemical structure and  $^1\text{H}$  NMR spectrum of APAB



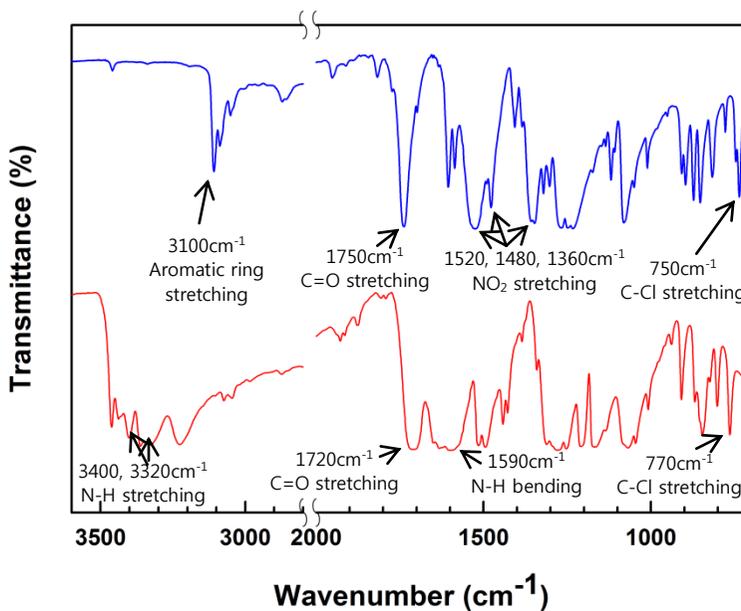
**Figure 3.3** Chemical structure and <sup>1</sup>H NMR spectrum of CNPNB



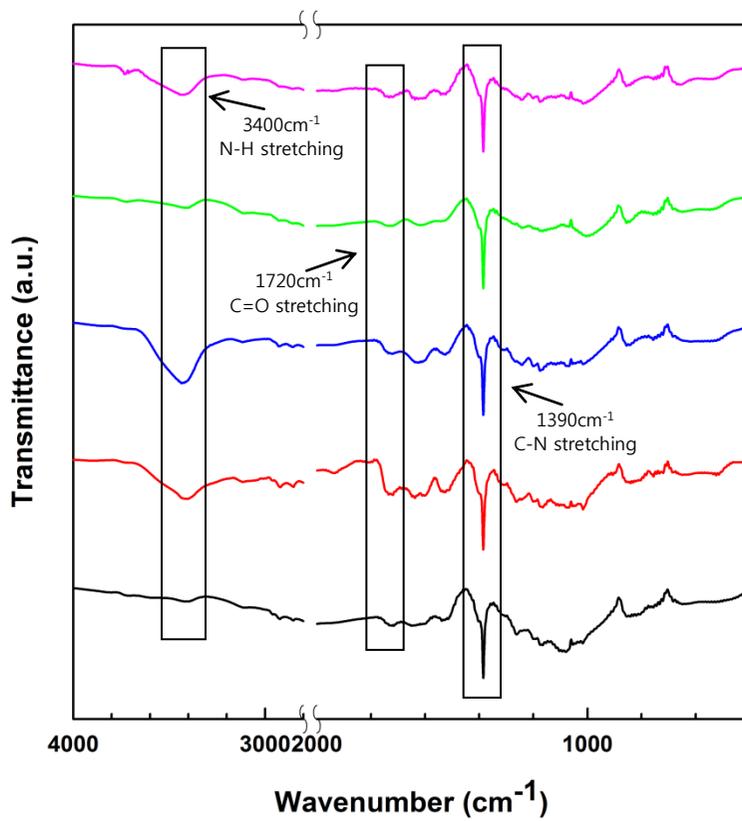
**Figure 3.4** Chemical structure and <sup>1</sup>H NMR spectrum of CAPAB



**Fig 3.5** FT-IR spectrum of NPNB(blue) and APAB(red)

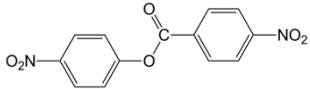
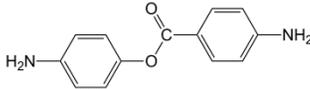
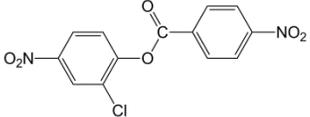
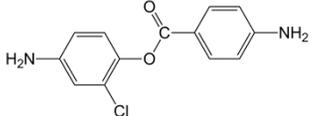


**Fig 3.6** FT-IR spectrum of CNPNB(blue) and CAPAB(red)



**Fig 3.7** FT-IR spectrum of aromatic poly(ester-amide)s; Cl 0 (black), Cl 25 (red), Cl 50 (blue), Cl 75 (green), Cl 100 (pink)

**Table 3.1** Results of elemental analyses of NPNB, APAB, CNPNB and CAPAB.

Chemical structure	Formula		C (wt%)	H (%)	N (wt%)	O (wt%) <sup>a</sup>	Cl (wt%) <sup>b</sup>
	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O <sub>6</sub>	Calc.	54.18	2.80	9.72	33.31	-
		Found.	54.35	2.77	9.55	33.33	-
	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	Calc.	68.41	5.30	12.27	14.02	-
		Found.	68.51	5.32	12.19	13.98	-
	C <sub>13</sub> H <sub>7</sub> ClN <sub>2</sub> O <sub>6</sub>	Calc.	48.39	2.19	8.68	29.75	10.99
		Found.	48.53	2.13	8.48	29.87	10.99
	C <sub>13</sub> H <sub>11</sub> ClN <sub>2</sub> O <sub>2</sub>	Calc.	59.44	4.22	10.66	12.18	13.50
		Found.	59.49	4.20	10.64	12.17	13.50

<sup>a</sup> The oxygen content was calculated from C,H,N elemental analysis. (wt % of O = 100 – wt% of C – wt% of H – wt% of N)

<sup>b</sup> The chlorine content was calculated from C,H,N and O elemental analysis. (wt % of Cl = 100 – wt% of C – wt% of H – wt% of N – wt% of O)

## 3.2 Optimized geometries

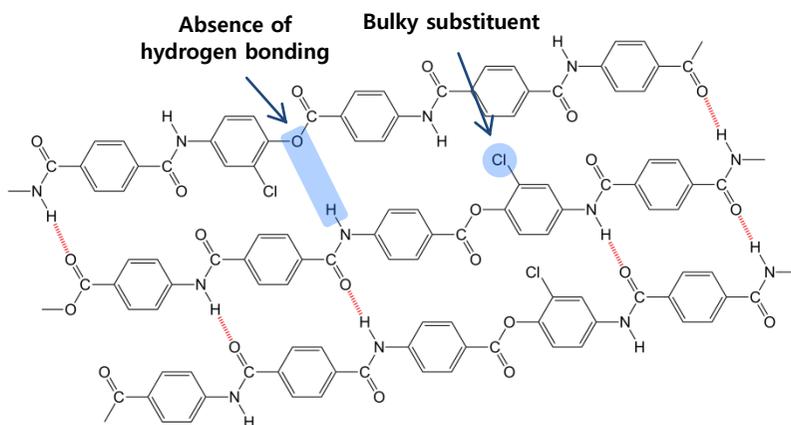
Aromatic polyamide chains are normally aligned parallel and influenced by inter-chain hydrogen bonding when the polymer solution exhibits liquid crystalline behavior. At this time, polymer chains must have the extended chain conformation, or rigid rod structure to show lyotropy. For that reason, it is important to simulate geometries of polymers to confirm the extended chain structure. If there is too much torsion on the repeating unit of polymers, chains have the helix structure which causes impossibility of lyotropy.

Fig 3.8 shows the expected geometries of the aromatic polyamide synthesized in here. Because there are many ester groups, the hydrogen bonding is not generated in several areas where ester groups exist. Furthermore, introduced chlorine groups act as a bulky separator between polymer chains to diminish the hydrogen bonding energy by increasing the length of it. Despite introducing ester and chlorine group, it is anticipated for aramid backbones to maintain the rigid structure and this prediction was ascertained by simulation.

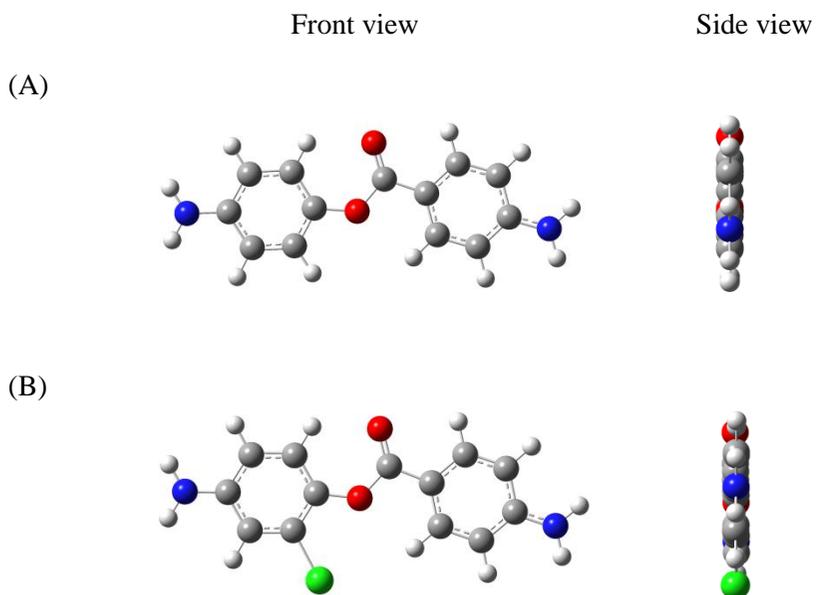
Meanwhile, optimized geometries of monomers and repeating units of polymers were obtained by computer simulation using density functional theory calculation method based on B3LYP function and 6-31G basis set. Fig 3.9 shows the optimized structures of two diamines (APAB, CAPAB). In the figure, it was confirmed that two benzene rings linked with one ester group in APAB and CAPAB maintained their planarity well. Thus, these monomers were expected not to disturb the extended chain conformation, only reducing

the number of hydrogen bonding. Likewise, the polymer synthesized from these aromatic diamines was expected to show the liquid crystalline behavior in the solvent.

Fig 3.10 shows the optimized structure of repeating units of APAB and CAPAB based homopolymers respectively. Because it is hard to investigate whole structure of the polymer, a repeating unit including one of two diamines and terephthalamide moieties was investigated each. Although there was torsion between amide group and benzene ring, moieties of the ester group was nearly planar in both monomers. (Angles between two benzene rings:  $0.787^\circ$  in case of APAB,  $2.52^\circ$  in case of CAPAB) Meanwhile, the torsion angle between two aromatic rings including the amide bond next to them was  $25.4^\circ$  in case of APAB polymer repeating unit and  $26.6^\circ$  in case of CAPAB polymer repeating unit each. From this data, introduction of bulky chlorine group does not exert a bad influence on liquid crystalline behavior and the ester group is an excellent moieties which promote the extended chain conformation of synthesized polymer backbones.



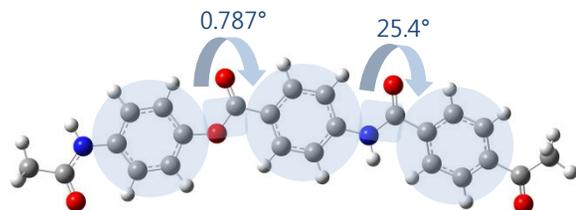
**Fig 3.8** Expected geometry of synthesized amamid backbone



**Figure 3.9** Optimized structure of APAB (A) and CAPAB (B)

(A)

Front view

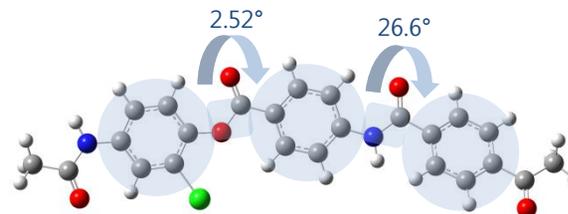


Side view

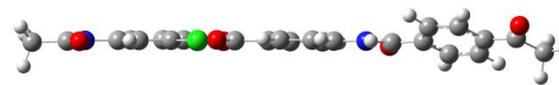


(B)

Front view



Side view



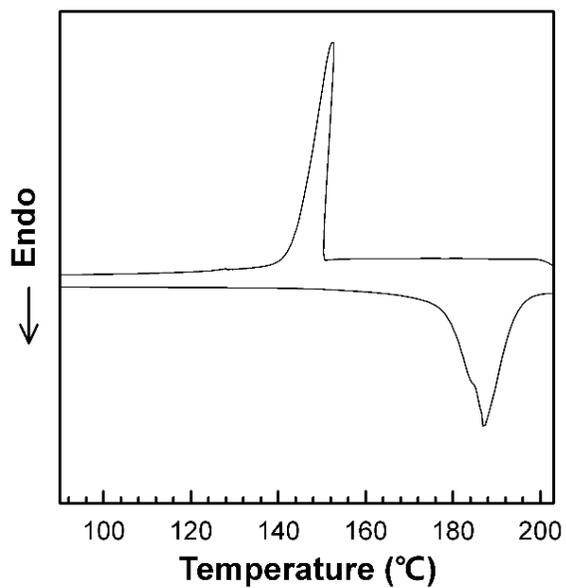
**Fig 3.10** Optimized structure of the repeating unit which shows it of APAB (A) and CAPAB (B) based polymer

### 3.3 Thermal properties

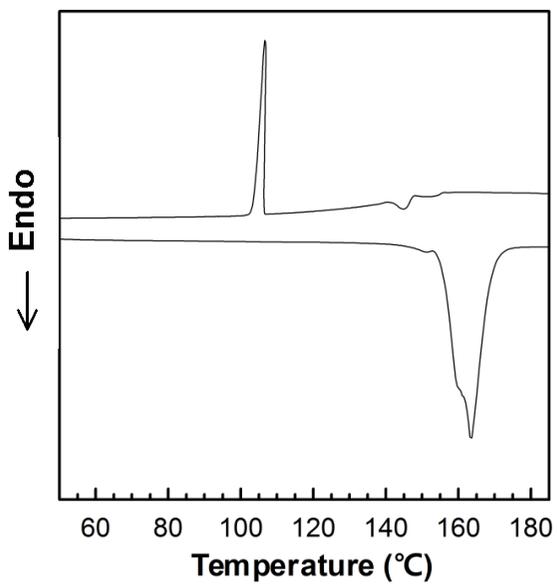
Thermal properties of synthesized monomers and polymers were investigated by DSC and TGA instrument. In the DSC data of fig 3.11, APAB exhibited a distinct endothermic peak at 187°C and exothermic peak at 152°C, while CAPAB exhibited a endothermic peak at 163°C and exothermic peak at 105°C in fig 3.12. The reason why both peaks of CAPAB are lower than APAB is because the conformation of it is slightly twisted by the bulky chlorine atom. From this data, it is expected that polymers synthesized from CAPAB would have great solubility through slight torsion of it more than ones synthesized from APAB. Another important thing is that each plot shows sharp exothermic peaks which indicate high crystallinity of monomers. In this case, the crystallinity is usually maintained even after the polymer is synthesized from each monomer which helps the exhibition of liquid crystalline behavior.

Meanwhile, fig 3.13 and 3.14 show TGA thermograms of monomers and polymers synthesized with various monomer ratios. In the monomer data, the aromatic diamines were degraded thermally at around 300°C. Although the degradation of chlorinated diamines started rapidly, the speed of degradation decreased sharply soon and it occurred through several steps. Because of this, final char yield was higher than APAB and it is considered that because halogen atom has flame-retardant nature. In case of polymers, it is confirmed that all copoly(ester-amide)s had good thermal stability without any significant weight loss up to 400°C under N<sub>2</sub> atmosphere. One thing to note is that the more the chlorine atom is included, the higher the char yield was

obtained. As the polymer contains more chlorine group, slight degradation started earlier, but the rate of it became slower. In DSC analysis, all the polymers did not show any transition because aromatic poly(ester-amide)s have very high melting temperature. Therefore, if aramids is heated continuously to melt down, the polymers would be decomposed before melting.



**Fig. 3.11** DSC thermogram of APAB



**Fig. 3.12** DSC thermogram CAPAB

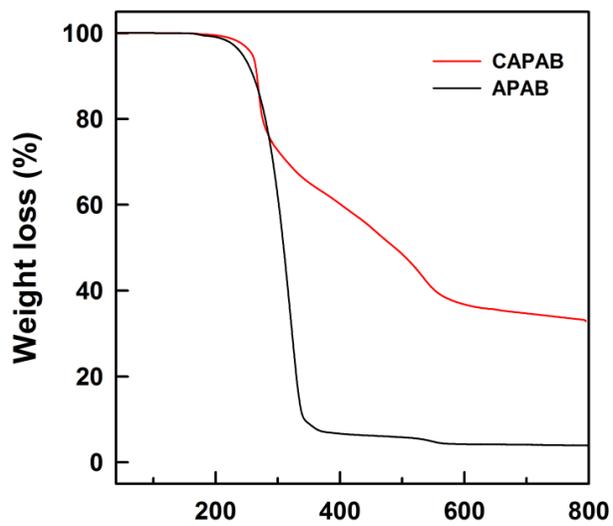


Fig. 3.13 TGA thermogram of monomers

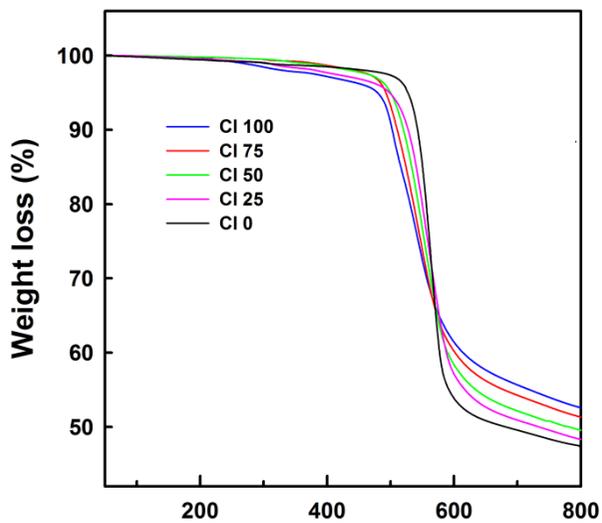


Fig. 3.14 TGA thermogram of polymers

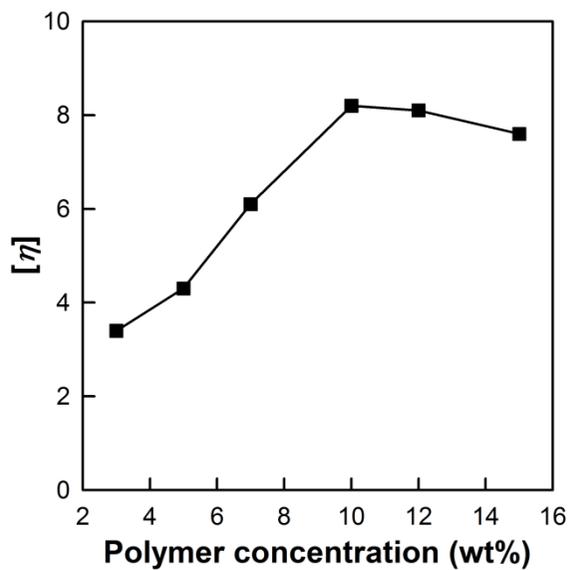
### 3.4 Polymerization conditions and solubility

In this study, polymerization was optimized with various conditions of polymer concentration, polymerization temperature and time, concentration of metal salt, addition time effect of neutralizing agent and the ratio of two aromatic diamines and after that, the intrinsic viscosity (I.V) values were measured and compared each other. J. Bao et al reported that the molecular weight of PPTA could be optimized to the highest value in the NMP+CaCl<sub>2</sub> system by adjusting polymerization conditions mentioned above.<sup>44</sup> In the report, the I.V value had optimized point among various concentrations of polymer weight and metal salt, but the stirring time was unrelated to it. Likewise, T. J. Oh et al reported that the high molecular weight of aromatic poly(ester-amide)s was obtained when TPC was added all at once, but the result was the reverse when TPC added slowly.<sup>38</sup> From this results, it is confirmed that the reaction of TPC with diamine is so fast that 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. And also, S. L. Kwolek et al reported that the momentary reaction by adding all of TPC quickly resulted in high molecular weight of polymer and narrow molecular weight distribution.<sup>17</sup> This coincides in opinion with uttered other reports above.

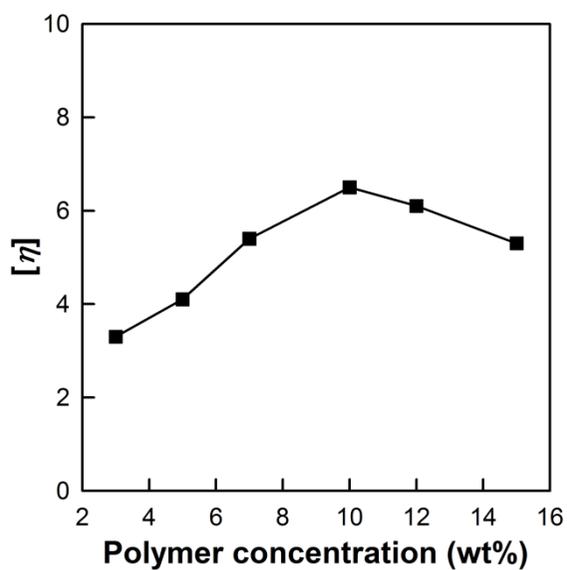
First of all, the effect of CAPAB and APAB polymer concentration on I.V values was investigated. As shown fig. 3.15 and 3.16, the highest molecular weight of polymers was obtained near at 10wt% each. As the polymer

concentration increased, I.V values also increased normally because the dense concentration make monomers to encounter more frequently and react each other easily. However, after reaching specific concentration, I.V values start to decrease. This is because the growth of polymer chain is limited due to the limitation of solubilizing power to solvent at high concentration.<sup>17,25,31,37,38</sup> Also, the high concentration of monomers results in rapid gelation of polymer solution before the polymer have high degree of polymerization which causes to hinder the access from the monomer to others. Lastly, the rate of side reaction become fast due to increasing heat of reaction resulting from reactions between 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 between diacid chlorides with the amide solvent (NMP in here), which result in relatively lower molecular weight polymers.

The notable difference between two data is the higher I.V value of CAPAB polymers. According to other reports, metal salt assists amine groups and acid chlorides to interact each other for the chemical reaction by electrical charge of salt ions as well as it helps polymers to dissolve well in organic solvents.<sup>38,45</sup> From this truth, it is expected that CAPAB would interact with ions more actively due to its electronegative chlorine atom and CAPAB polymers would have higher molecular weight than APAB polymers.



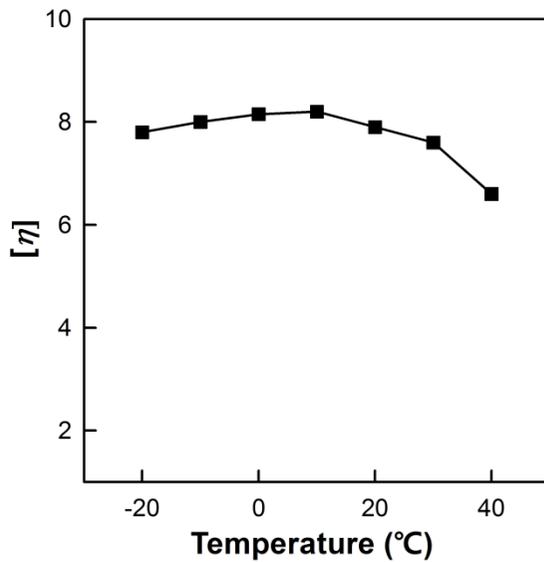
**Figure 3.15** Effect of CAPAB polymer concentration on I.V  
(metal salt: 2%)



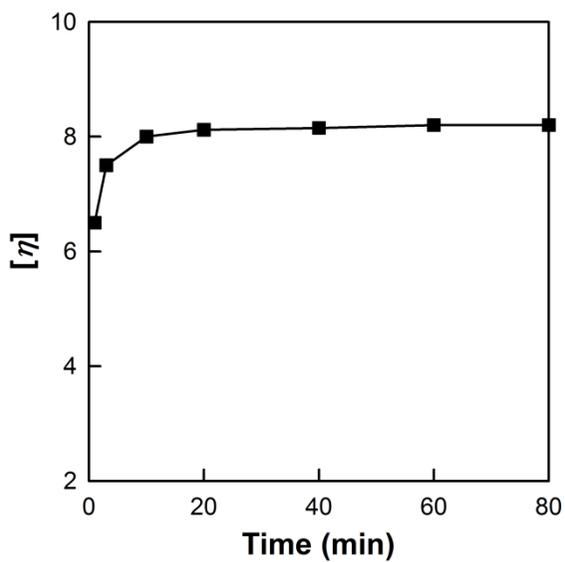
**Figure 3.16** Effect of APAB polymer concentration on I.V  
(metal salt: 2%)

Next, the effect of temperature and reaction time on polymer molecular weight was investigated respectively. As shown in fig 3.17, the temperature between  $-20$  to  $10^{\circ}\text{C}$  did not affect much on the molecular weight of the polymers, but as the temperature increase, the molecular weight began to decrease. P. W. Morgan reported that polycondensation between diamine monomers with diacid needs low temperature to obtain high molecular weight polymers because the reaction is exothermic and the oxidation of diamine is prevented at the low temperature. Like this precedent, CAPAB polymerization was optimized at the low temperature lower than  $10^{\circ}\text{C}$ . The higher temperature aroused decrease of I.V due to the heat of reaction and oxidation of diamine. At the temperature nearly  $-20^{\circ}\text{C}$ , I.V was lower than upper temperature because the reaction rate is dependent on a temperature. Therefore, if the reaction keeps progressing for a long time, I.V would be higher similarly with one at  $0\sim 10^{\circ}\text{C}$ .

The relationship between reaction time and I.V was also investigated. In the fig 3.18, the I.V value reached at the highest level within 20 minutes. This is the average time for aromatic poly(ester-amide)s to have the largest molecular weight. After that, there was very slight difference about it even the reaction continued until 80 minutes.

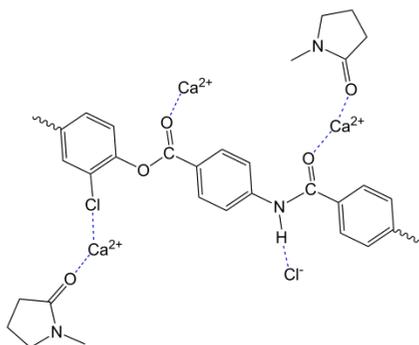


**Figure 3.17** Effect of temperature on I.V  
(metal salt: 2%, CAPAB polymer concentration: 10wt%)



**Figure 3.18** Effect of reaction time on I.V  
(metal salt: 2%, CAPAB polymer concentration: 10wt%)

The effect of metal salt was also investigated by adjusting its concentration. When the metal salt is added in the amide solvent like DMAc or NMP, a complex between metal salt ion and a solvent molecule generates, which results in greatly enhanced solubilizing ability. LiCl, CaCl<sub>2</sub> is used as the metal salt usually in the preparation of aromatic polyamides. This complex stabilizes the polymerization intermediate which results in the high degree of polymerization and helps the polymer to dissolve in the solvent.<sup>38,45</sup>



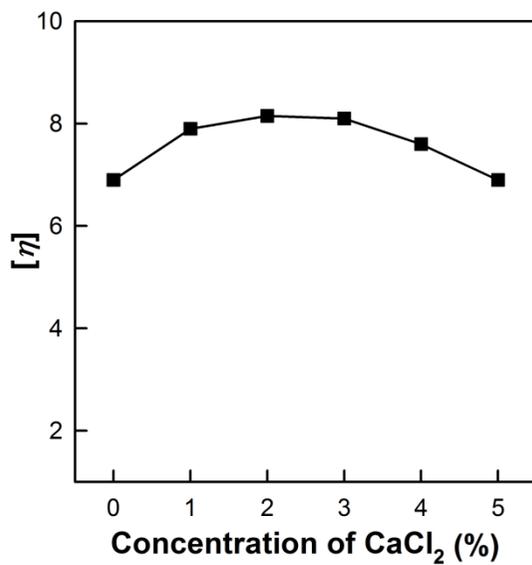
**Fig 3.19** Interaction among the polymer, metal salt and solvent

As shown fig 3.19, ions from metal salt can interact with both polymer and solvent. Electronegative chlorine atom and oxygen atom can interact with calcium cation by their lone pair electron and proton in amide group also can interact with electronegative chlorine anion. Through this complexation, the polymer is able to dissolve in amide solvent well. In this case, because the inter-chain hydrogen bonding of polymer backbone is interrupted by salt ions and the salt-solvent complex can interact with the polymer chain more favorably than the pure solvent alone, the solubility of solvent is excellently

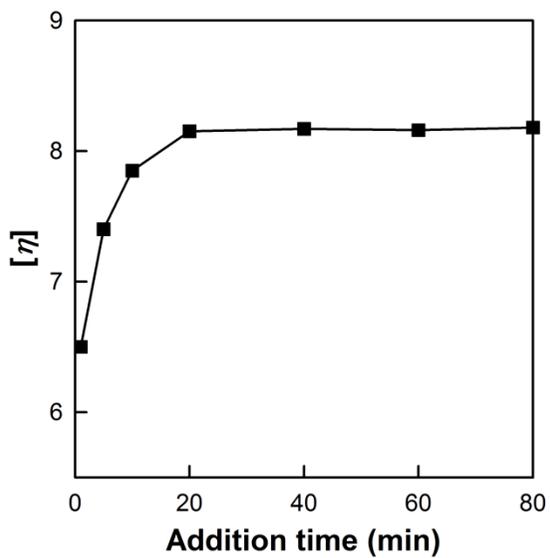
enhanced. But, at high concentration of metal salt, the cation interacts with the carbonyl oxygen in amide of polymer backbone directly than the carbonyl oxygen of solvent. Thus, the solubility of solvent to polymer could not be enhanced effectively. Thus, there can be an optimum amount of metal salt when it is used in the polymerization.

Fig 3.20 shows the effect of  $\text{CaCl}_2$  concentration on the I.V. Since the maximum solubility of  $\text{CaCl}_2$  in NMP is only 6% (6 g per 100 ml solvent) at  $20^\circ\text{C}$ , this experiment was carried up to 5% of  $\text{CaCl}_2$ . When the polymerization progressed without metal salt, the I.V value was only 6.9, but as the amount of salt increase, I.V value also increased until 2% of  $\text{CaCl}_2$ , followed by decrease of it after 2%. From the 4% concentration, the I.V value critically decreased because too much amount of salt disturbs the reaction between reactants. As a result the optimized concentration of salt was confirmed to 2%.

The addition time of neutralizing agent was also optimized in sequence. After TPC was added, the polymer solution became high viscous gel or solid above 7wt%. At that time, calcium oxide ( $\text{CaO}$ ) was used to neutralize hydrogen chloride generated during the polymerization.  $\text{CaCl}_2$  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 the fig 3.21, the optimized addition time of  $\text{CaO}$  was shown. When the  $\text{CaO}$  was added as soon as the reaction started, the molecular weight of polymer was very low comparing with other values.



**Fig 3.20** Effect of CaCl<sub>2</sub> concentration on I.V  
(polymer concentration: 10wt%, temperature: 5 °C)



**Figure 3.21** Effect of addition time (CaO) on I.V  
(metal salt: 2%, CAPAB polymer concentration: 10wt%)

This phenomenon can be explained by the chemical reaction of the neutralizing agent. In the chemical reaction equation of it ( $\text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$ ), addition of CaO induces the generation of water molecules which have the latent possibility to act as an oxidant of diamines, so CaO needs to be added as late as possible. In the data, the I.V value maintained the highest level since the addition at 20 minutes. That is because most monomers are reacted within 20 minutes as mentioned above, so generated water during neutralization does not have a bad effect on the molecular weight.

Next experiments were carried based on the previous results. We focused on preparation of the anisotropic polymer dope directly after the neutralization in NMP +  $\text{CaCl}_2$ . Because liquid crystalline behavior is depending on the polymer concentration, only this condition was changed and at the same time, other factors were fixed. (metal salt: 2%, polymerization temperature: 5°C, CaO equivalent with generated HCl used after the solidification of polymer solution)

Table 3.2 shows the final dope state and the optical anisotropy of CAPAB homopolymers with various polymer concentrations after neutralizing with CaO. At the low concentration below 5%, the optical anisotropy of the polymer solution was not observed. On the other hand, at higher concentration more than 7%, dopes were exhibited optically anisotropic properties. Although the neutralizing agent was added after 20 minutes, the solidified polymer dopes did not become solution. Therefore, It was considered because the molecular weight of the polymers was too high. It is thought that the great solubility of CAPAB polymers during polymerization causes too high values.

**Table 3.2** CAPAB based homopolymer with various polymer concentration (wt%)

<b>Polymer concentration (wt%)</b>	<b>Final dope state</b>	<b>Optical anisotropy</b>	<b>I.V</b>
15	Solid	O	7.6
12	Solid	O	8.1
10	Solid	O	8.2
7	Gel	O	6.1
5	Solution	X	4.3
3	Solution	X	3.4

Metal salt: 2%, polymerization temperature: 5 °C, Final dope state was determined after neutralizing with CaO.

**Table 3.3** CAPAB based homopolymers of which molecular weight was controlled by TPC feed ratio

<b>Polymer concentration (wt%)</b>	<b>TPC feed ratio</b>	<b>Final dope state</b>	<b>Optical anisotropy</b>	<b>I.V</b>
10	1	Solid	O	8.2
	0.96	Solid	O	5.8
	0.94	Solid	O	4.6
	0.92	Gel	O	3.9
	0.9	Gel	O	3.5

'TPC feed ratio' means ratio of TPC to diamine, metal salt: 2%, polymerization temperature: 5 °C, neutralized with CaO.

Thus, TPC feed ratio to diamine was reduced from 1 equivalent to 0.9 while the polymer concentration was fixed with 10wt%.

Table 3.3 shows dope states and optical anisotropy results which are controlled TPC feed ratio. In condensation polymerization, the ratio between the monomers largely affects the final molecular weight of polymer. The more the mole ratio of monomers goes to nearly one, the higher molecular weight of polymer can be obtained. Thus, it was expected that lower feed ratio of TPC would bring the lower molecular weight of polymer, which enable to prepare the anisotropic polymer dope. As shown table 3.3, there was a dramatic decrease in I.V when the 0.9 equivalent of TPC was fed. But, due to the very low molecular weight, the optical anisotropy didn't show up. From this result, the polymer dope with exhibiting optical anisotropy in the liquid state could not be obtained in CAPAB based homopolymer system. Although hydrogen bonding was interrupted by ester group and chlorine substituent, the polymers were insoluble in organic solvents due to the regularity of polymer backbone and too many chlorine atoms.

Therefore, non-chlorinated APAB monomer was introduced. When the 2 aromatic diamines, CAPAB 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 3.4 and 3.5 shows the change of I.V values in APAB based homopolymer system according to the change of polymer concentration and TPC feed ratio respectively. In case of polymerization of table 3.4, the tendency of results was similar with results of CAPAB homopolymers.

**Table 3.4** APAB based homopolymer with various polymer concentration (wt%)

<b>Polymer concentration (wt%)</b>	<b>Final dope state</b>	<b>Optical anisotropy</b>	<b>I.V</b>
15	Solid	O	5.3
12	Solid	O	6.4
10	Solid	O	6.5
7	Gel	O	5.4
5	Solution	X	4.1
3	Solution	X	3.3

Metal salt: 2%, polymerization temperature: 5 °C, Final dope state was determined after neutralizing with CaO.

**Table 3.5** APAB based homopolymers of which molecular weight was controlled by TPC feed ratio

<b>Polymer concentration (wt%)</b>	<b>TPC feed ratio</b>	<b>Final dope state</b>	<b>Optical anisotropy</b>	<b>I.V</b>
10	1	Solid	O	6.5
	0.96	Solid	O	5.1
	0.94	Solid	O	4.4
	0.92	Gel	O	3.6
	0.9	Solution	O	3.0

'TPC feed ratio' means ratio of TPC to diamine, metal salt: 2%, polymerization temperature: 5 °C, neutralized with CaO.

There was also exhibition of lyotropy above 7 wt% and anisotropic dope states were all solid. It was noticeable that relatively lower molecular weights of polymers were obtained compared to CAPAB based homopolymer system although the same polymerization conditions were applied. This was because the solubility of CAPAB based homopolymer was higher than APAB based homopolymer as mentioned above. In case of APAB polymers, it was hard to be the solution state despite the lower molecular weight more than CAPAB polymers because APAB polymers have the more rigid and planar structure.

In the table 3.5, when TPC feed ratio was 0.9 equivalent, the final dope state of APAB homopolymer was solution while the final dope state of CAPAB homopolymer was gel. In case of APAB based homopolymer which polymerized with 0.9 equivalent of TPC, the anisotropic polymer dope in liquid state was obtained. When the TPC feed ratio was above 0.94 equiv, the solution state was not obtained due to the high molecular weight and the regularity conformation likewise with CAPAB based homopolymer. Although the polymer dope with optical anisotropy was obtained like above, its molecular weight was too low to be spun in fibers with excellent mechanical properties. When the polymer dopes having I.V value below 3.0 were spun, the filament would be broken easily due to the low molecular weight of the polymer.

For any solution spinning process, there are several requirements. Firstly, the molecular weight of polymer should be as high as possible to maximize the mechanical properties. Secondly, dope viscosity should be high to aid processability of polymers. Lastly, the polymer concentration should be high

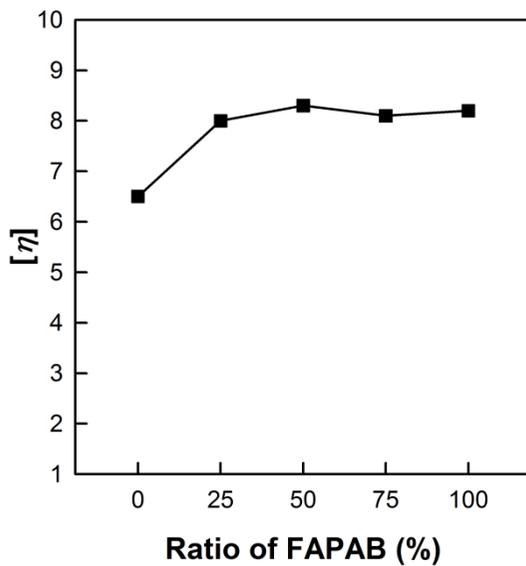
to minimize the cost of solvent. In case of APAB homopolymers, the polymer dope soluble in NMP+CaCl<sub>2</sub> solution which exhibits optical anisotropy were obtained by TPC feed ratio control, but the dope was not suitable for the spinning due to its low molecular weight. Thus, for the spinning of the polymer dope, the molecular weight of aromatic poly(ester-amide)s should be increased while the dope maintains the solution state. Therefore, copolymerization of CAPAB and APAB was progressed. It was expected that the random distribution of CAPAB and APAB moieties through the backbone offers an increased solubility in organic solvents. It was anticipated that only a small quantity of chlorine atom would break a rigid structure of APAB polymers and increase the length between polymer chains.

Fig 3.22 and table 3.6 shows I.V values and dope states of poly(ester-amide)s with different feed ratio of CAPAB and APAB from Cl 0 to Cl 100. In the data, once CAPAB was used as the monomer, the I.V values of polymers were increased markedly. This indicated that even a small portion of CAPAB moiety can help to increase the solubility during the polymerization which gives growing polymer chains the mobility in the solution and to obtain the high molecular weight of polymers. However, despite this result, the dope state still remained solidified after using the neutralizing agent. Therefore, TPC feed ratio control was introduced likewise.

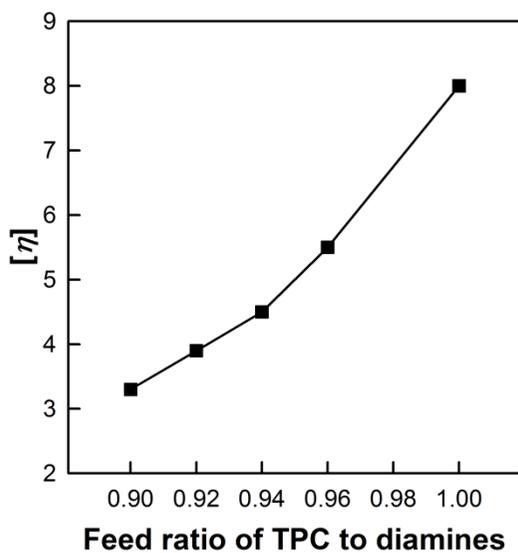
Before starting it, the fixed feed ratio of diamine was determined to 25 percent of CAPAB and 75 percent of APAB. That is because raw materials of APAB are much cheaper than ones of CAPAB, so productivity of it was higher. As shown fig 3.23 and table 3.7, the optically anisotropic solution with

the molecular weight of I.V 4.5 could be prepared in Cl25 copolymer. Although this copolymer has higher molecular weight than CAPAB or APAB homopolymers, the optically anisotropic polymer maintained the state of solution. This was because the solubility of copolymer was enhanced by random copolymerization and small amount of chlorine substituent.

Lastly, solubility of CAPAB and APAB copolymers was investigated. In case of DMF, THF, chloroform, every polymer could not dissolve in there. Even DMAc and NMP were unable to dissolve copolymers perfectly even by heating except for APAB homopolymer which is hard to dissolve in many organic solvents because of its rigid structure. After adding the metal salt in amide solvents (CaCl<sub>2</sub> to NMP, LiCl to DMAc) polymers could dissolve in that solvents, but only APAB homopolymers needed heating. The notable point is that all polymers having chlorinated monomer moieties could dissolve easily regardless of the amount of added CAPAB. This represents the excellent solubility of polymers can be obtained even addition of CAPAB with the 25% ratio of all diamines.



**Fig 3.22** Effect of CAPAB ratio on the molecular weight of copolymers (Metal salt: 2%, polymer concentration: 10wt%)



**Fig 3.23** Effect of TPC feed ratio on I.V in copolymer system (CAPAB:APAB=25:75, metal salt: 2%, polymer concentration: 10wt%)

**Table 3.6** APAB based homopolymer with various polymer concentration (wt%)

Polymer concentration (wt%)	Diamine feed ratio		Final dope state	Optical anisotropy	I.V
	CAPAB	APAB			
10	0	100	Solid	O	6.5
	25	75			8.0
	50	50			8.3
	75	25			8.1
	100	0			8.2

Metal salt: 2%, polymerization temperature: 5 °C, Final dope state was determined after neutralizing with CaO.

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

Polymer concentration (wt%)	TPC feed ratio	Final dope state	Optical anisotropy	I.V
10	1	Solid	O	8.0
	0.96	Gel		5.5
	0.94	Solution		4.5
	0.92	Solution		3.9
	0.9	Solution		3.3

Metal salt: 2%, polymerization temperature: 5 °C, Final dope state was determined after neutralizing with CaO.

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

Polymer	I.V	NMP + CaCl <sub>2</sub> 5%	DMAc + LiCl 5%	NMP	DMAc	DMF	THF	CHCl <sub>3</sub>
Cl 0	6.5	O	O	X	X	X	X	X
Cl 25	8.0	OO	OO	△	△	X	X	X
Cl 50	8.3	OO	OO	△	△	X	X	X
Cl 75	8.1	OO	OO	△	△	X	X	X
Cl 100	8.2	OO	OO	△	△	X	X	X

Polymer concentration: 0.5g/dL, temperature: 40 °C

OO: soluble, O: soluble by continuous heating, △: partially soluble even by continuous heating, X: insoluble

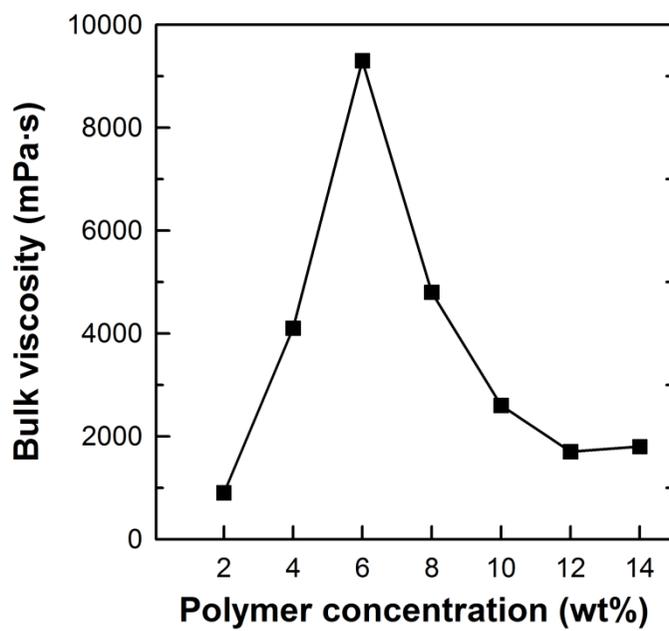
### 3.5 Liquid crystalline behavior

Liquid crystalline behaviors of the synthesized aromatic poly(ester-amide)s were investigated by polarized optical microscope (POM) image and Brookfield viscometer. In these observations, Cl 25 copolymer dope with various polymer concentration synthesized by 0.94 equivalent TPC were investigated. The measurement of bulk viscosity of polymer dope, the bulk viscosities were obtained from each polymer concentration using Brookfield viscometer and POM images were obtained at each concentration from low to high concentration.

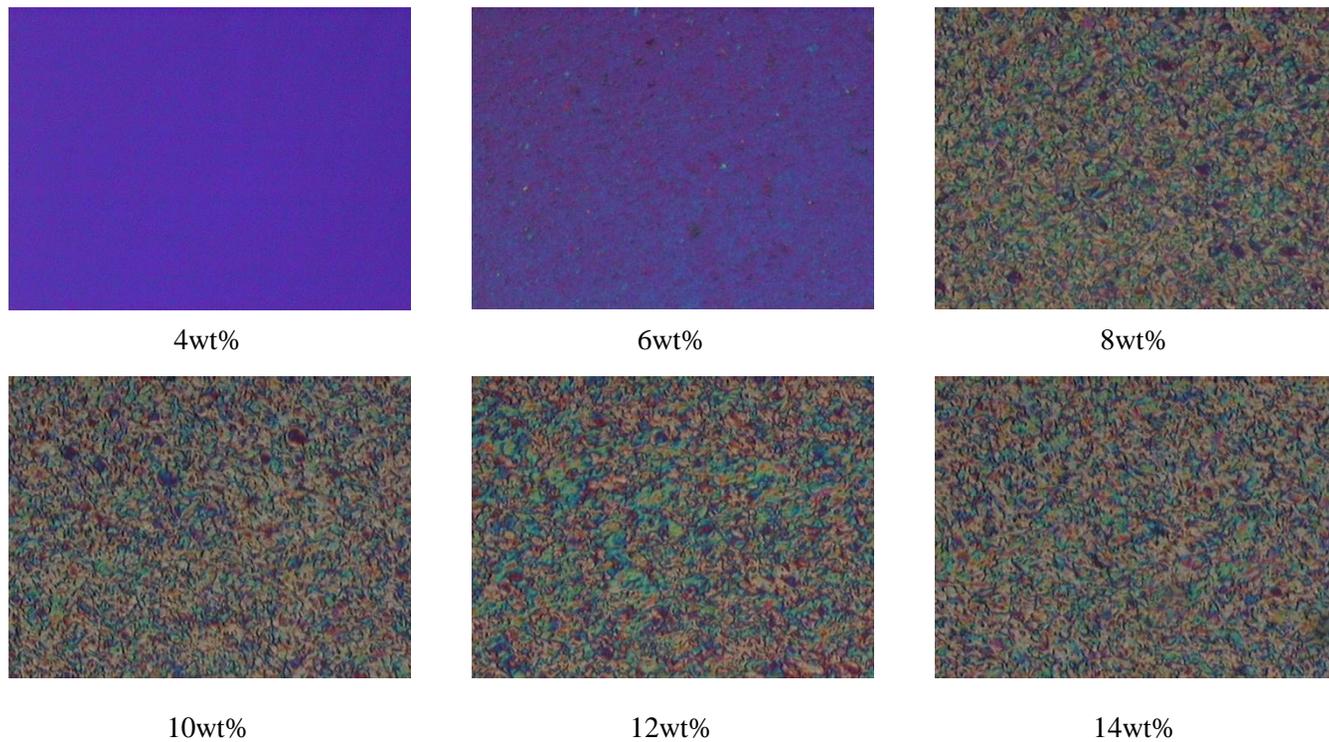
Fig 3.24 shows the change of the bulk viscosity of Cl 25 copolymer solution depending on the polymer concentration. Until the viscosity reaches at 6wt% concentration, the bulk viscosity was increased with the rise of polymer concentration similar to the general isotropic polymer solution. At the point at 6wt%, the polymer solution was very viscous and its bulk viscosity was highest as 9300 mPa·s among other samples, so-called critical concentration. However, as go to the higher concentration, the optical anisotropy began to appear and the viscosity also started to decrease rapidly up to 1700 mPa·s at 12wt% since critical concentration which 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 polymers start to align parallel to each other to

diminish the friction between them when it flows in the solution, which results in the formation of nematic liquid crystalline behavior. Because the slippage of the liquid crystal domain occurred more easily under liquid crystalline state, the bulk viscosity is lower after the critical concentration.

Meanwhile, Fig 3.25 shows POM images of Cl 25 polymer solution with various polymer concentrations. At 4wt%, no liquid crystal was observed, but the liquid crystal started to form at 6wt% gradually. The clear nematic texture could observe from 8wt%. Therefore, it is expected that the accurate critical concentration of Cl 25 would be the value of 6wt% or slightly more than it from the images.



**Figure 3.24** Bulk viscosity of Cl 25 copolymer solution



**Fig 3.25** POM images of Cl 25 copolymer solution

## Chapter 4. Conclusion

In this study, two aromatic diamines CAPAB and APAB containing ester group and chlorine substituent were designed and synthesized. An also aromatic poly(ester-amide)s from the synthesized aromatic diamines polymerized and it was investigated to have good thermal stability and lyotropic in the organic solvent. In CAPAB and APAB homopolymer systems, the corresponding poly(ester-amide)s exhibited liquid crystal formation respectively, but it was hard to obtain the anisotropic polymer solution with high molecular weight due to their low solubility in organic solvents resulting from their regularity. To break it and enhance the solubility of polymer in organic solvents, random copolymerizations were progressed to synthesize polymers consisting of CAPAB and APAB monomers with various mole ratio. As results, the solubility of copoly(ester-amide)s was quite increased. In particular, under the condition of monomer concentration 10wt%, metal salt 2%, 0.94 equivalent of TPC feed ratio and the diamine composition of CAPAB 25%, APAB 75%, the polyamide which have moderate molecular weight of I.V 5.0 could be obtained and the optically anisotropic polymer solution was prepared in the NMP solvent added with metal salt. After investigation of its bulk viscosity, the critical concentration was revealed to 6wt% which is the point of starting the formation of liquid crystalline behavior. This was also proved by POM images and the nematic texture was distinctly observed from 8wt% concentration.

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## 초 록

방향족 폴리아미드는 수십 년 간 이들의 우수한 내열 특성과 기계적 물성을 응용하기 위해 연구되어왔다. 하지만 고분자 사슬간의 강력한 수소결합에 기인하여 유기용매에 대한 이 고분자 용해성은 낮은 편이었고, 이러한 점 때문에 고분자의 가공 및 사용이 제한되어 왔다. 따라서 본 연구에서는 이 문제를 해결하기 위해 화학적 변형이 가미된 새로운 방향족 폴리아미드를 디자인하고 합성하였다. 특히, 폴리아미드를 중합하는데 사용되는 방향족 다이아민에는 수소결합의 밀도를 줄이고자 에스터 그룹이, 고분자 사슬간의 거리를 넓히고 수소결합 길이를 늘리고자 다소 커다란 크기의 클로린 치환체가 도입되었다. 그러나 단일 중합 시스템만으로는 수소결합 밀도가 감소하더라도 반복단위가 어느 정도의 규칙성을 가지므로 유기용매에 대한 용해도가 좋지 않아 중화제를 투입하여도 용액상태의 도프를 얻어내지 못하였다. 따라서 클로린 치환체의 도입 유무가 다른 두 종류의 다이아민 단량체를 공중합하여 고분자 내 반복단위의 규칙성을 감소시킴으로써 유기용매에 대한 용해성을 향상시키고자 하였다. 그 결과, CAPAB 기반 반복단위의 더 높은 용해성을 통해 적정 수준의 분자량을 가지면서 동시에 이방성 고분자 용액 상태를 유지하는 도프를 제조할 수 있었다. 이 용액은 6wt% 에서 Critical concentration을 갖고 이후의 고분자 농도부터 점도가 감소하는 것을 통해 특정 농도 구간에서의 액정성 발현이 증명되었다.

주요어: 아라미드, 방향족 폴리아미드, 용해성, 유기용매, 액정, 유방성

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