**Preparation of a transparent polyimide film using a truxinic acid derivative**

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## 1.Introduction

Plastic production volume in 2014 will exceed 10 million tons, and the day that is not in the eyes in everyday is not, it is the presence that is inseparable for our life. Plastic is made mainly from by-product of petroleum refining, increase in fossil fuel use along with the demand , and a happen depletion of fossil fuels. In addition, the rise of carbon dioxide concentrations generated by the combustion such as fossil fuel is considered as one of the causes of global warming, a breakaway from fossil fuel and the use expansion of the renewable resource are essential in sustainable social realization. Development of plastic is important that the substance to be produced as a raw material by the metabolism of the organism. Bio-based plastic has been desired, differently from biofuel development to achieve a carbon neutral cycle where $CO_2$ amount was not reduced in the atmosphere. On the other hand, semi-permanent carbon stock that reduces $CO_2$ in the atmosphere is thought to be able to reduce $CO_2$ by synthesizing highly durable bio-based plastics from biological resource. This is an important concept of carbon minus. I am focusing on super-engineering plastics, especially polyamides containing aromatic ring because they have high thermal, mechanical, and chemical-resistant properties.

Aromatic polyamide Kevlar has the best properties of all the conventional polyamides and consists of *p*-phenylene diamine and terephthalic acid dichloride. Aromatic diamine is important to synthesize high performance polyamide, but it is a problem that living organisms difficultly produce the diamines. Then, I focus dimerization of 4-aminocinnamic acid that can be obtained in biosynthetic route. Cinnamic acid is widely known as a photoreactive chemical compounds, it shows isomerization and cycloaddition. Our laboratory already reported it bout the synthesis of polyamide using the $\alpha$-truxillic acid derivative which is head-tail type dimer. However, the brittle it is a disadvantage in hard because there is a high axially symmetric. Generally, In general, in order to reduce the symmetry, molecular design for reducing the structural regularity is performed by copolymerization, bent structure, part of the side chain introduction. In this research, I synthesis of $\beta$-truxillic acid derivatives which is head- head type, and to perform the synthesis and physical properties of the new bio-based polyamide obtained by introducing a bent structure and flexible aliphatic into the molecule by using the synthesized monomers.

## 2. Experimental

2-1 synthesis of monomers

2-1-1 synthesis of 4-nitrocinnamic acid (4NCA) (1)

4ACA(0.74 g, 4.53 mmol), water(32 ml) and excess of potassium peroxymonosulfate(6.27 g, 10.2 mmol) was added to round-bottomed flask and mixture to refluxed for 5 hours. Formed precipitate

was filtered and dried in vacuo. The crude product was soxhlate extraction with 1,4-dioxane. Then removed the solvent to obtain a yellow powder (0.80 g, 88.9%)

2-1-2 synthesis of 4-nitrocinnamic acid methyl ester (4NCAMe) (2)

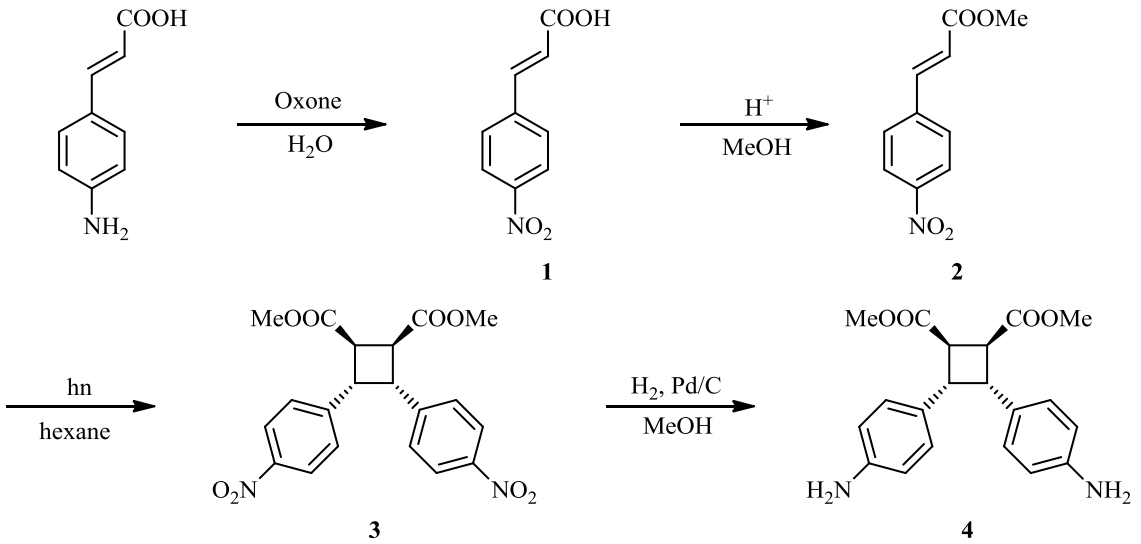
Concentrated sulfuric acid(6.3 ml) was added dropwise to methanol (200 ml) solution of 4NCA(25.29 g, 0.1309 mol). Allow the mixture to reflux for 3 hours. Formed precipitate was filtered and dried in vacuo. The obtained a slight yellow powder (26.78 g, 98.7%). Then, the product was recrystallized with hexane and ethyl acetate, filtered and dried in vacuo. The obtained a slight yellow crystals (23.64 g, 87.1%).

2-1-3 synthesis of 4, 4'-dinitro-*β*-truxinic acid dimethyl ester (*β*DNTAMe)(3)

Hexane dispersion (50 ml) of **2** (2.03 g, 9.80 mmol) was placed in round-bottom flask and irradiated UV using 250-450 nm Mercury lamp for 4 hours. Formed precipitate was filtered and dried in vacuo, the obtained a slight yellow powder (1.96 g, 96.6%). Then, the product was recrystallized with methanol filtered and dried in vacuo. The obtained a slight yellow crystals (1.77 g, 87.2%).

2-1-4 synthesis of 4, 4'-diamino-*β*-truxinic acid dimethyl ester (*β*DATAMe) (4)

The compound **3** (1.64 g, 3.96 mmol), 5%Pd/C (0.45 g, 0.05 mol%) and methanol (60 ml) was added to round-bottomed flask. The mixture was magnetically stirred and hydrogen reduction reaction at 50 ℃ for 1.5 hours.

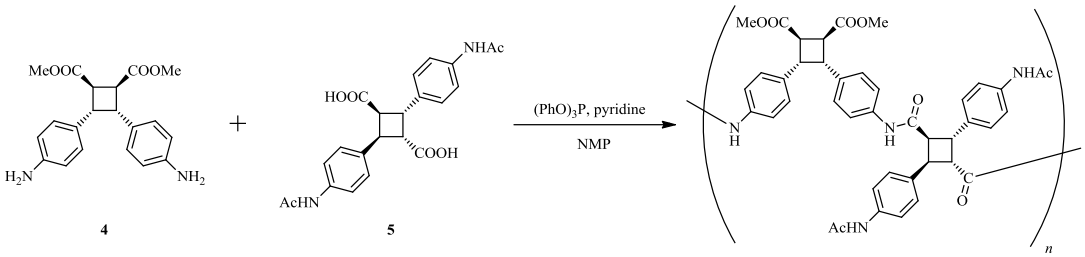



Scheme 1. Syntheses of , 4'-diamino-*β*-truxinic acid dimethyl ester

2-2 synthesis of polymers

2-2-1 synthesis of poly{(4, 4'-diyl-*β*-truxinic acid dimethyl ester) 4, 4'-diacetamido-*α*-truxillamide}

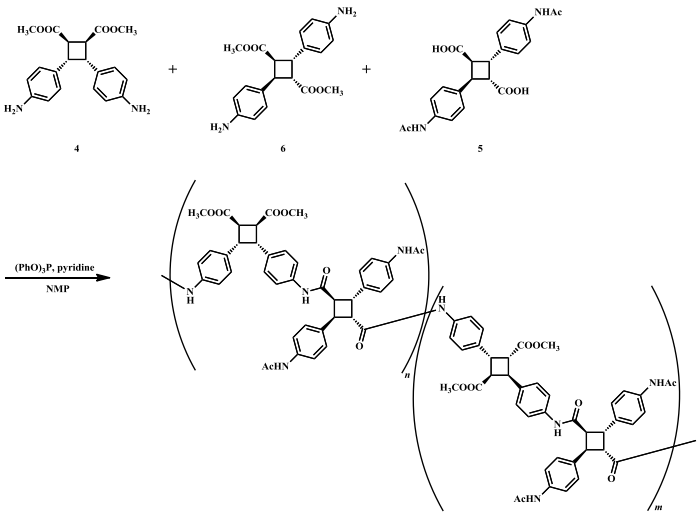
To **4** (99.39 mg, 0.28 mmol) and 4,4'-diacetamide-*α*-truxillic acid (*α*DACTA) (**5**) (114.95 mg, 0.28 mmol) placed in flask, N-methylpyrrolidone (NMP) (0.28 ml), tripheylphosphite (80 μl, 0.305 mmol) and pyridine (0.14 ml, 1.74 mmol) were added. After the reaction mixture was stirred for 15 hours at 110 ℃, the solution was diluted N, N-dimethylformamide (DMF) (0.28 ml) , then added dropwise into water (25 ml) To precipitate target polymer which was collected filtration and dried in reduced pressure (0.62g, 96.1%).




Scheme 2. Synthesis of poly{(4, 4'-diyl-*β*-truxinic acid dimethyl ester) 4,4'-diacetamido-*α*-truxillamide}.

2-2-2 synthesis of poly *β*DATAMe-*α*DATAMe-*α*DACTA

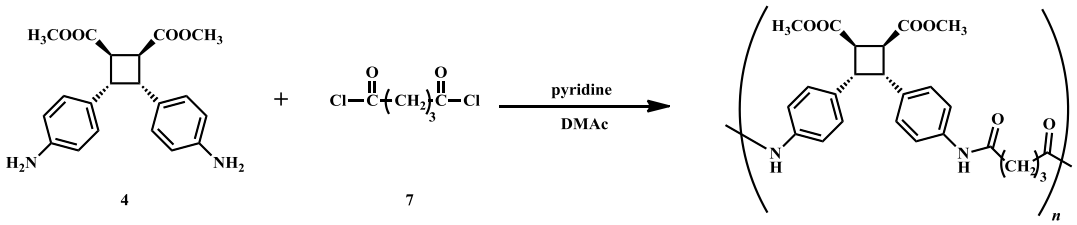
To **4**, **5** (0.29 mmol ) and 4, 4'-diamino-*α*-truxillic acid dimethyl ester(*α*DATAMe) (**6**) placed in flask, NMP (0.28 ml), tripheylphosphite (80 μl, 0.305 mmol) and pyridine (0.14 ml, 1.74 mmol) were added. After the reaction mixture was stirred for 15 hours at 110 ℃, the solution was diluted DMF , then added dropwise into water to precipitate target polymer which was collected filtration and dried in reduced pressure. The amount of **4** are equivalent to 25, 50, 75 mol% of **5**, the amount of **6** are equivalent to 75, 50, 25 mol% of **5**.




Scheme 3. Synthesis of poly (*β*DATAMe-*α*DATAMe-*α*DACTA).

2-2-3 Synthesis of poly{(4 4'-diyl-*β*-truxinic acid dimethyl ester) α,ω alkyloylamide}

To each solution of **4** in dry *N*, *N*-dimethylacetamide (DMAc) (200 μl~300 μl), each chloride (50 μl) was added dropwise, and stirred for 15 hours under nitrogen atmosphere. The amount of **4** corresponds to each amount of chloride.




Scheme 4. Synthesis of poly{(4,4'-diyl-*β*-truxinic acid dimethyl ester) 1,5'gurutarylamide}

## 3.Results and discussion

3-1 Synthesis of monomers

Photodimer obtained by photoreaction as shown in Scheme 1 was confirmed to be the *syn* head-head type the desired product by NMR, mass spectroscopy and four-axis X-ray diffraction.

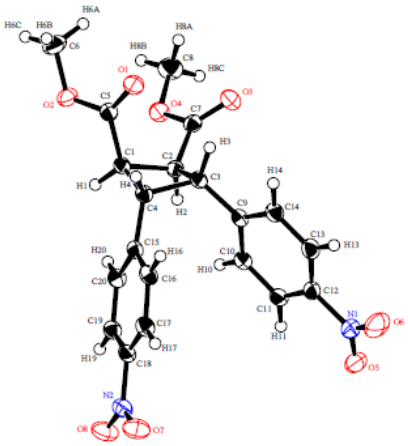


Figure 1. X-ray structure of 4,4'-dinitro-*β*-truxinic acid dimethyl ester.

3-2 Synthesis and molecular characterization of polyamides

3-2-1 Synthesis of Aromatic polyamides

Aromatic polyamides were prepared from **4**, **5**, **and 6** in Experimental section. The structures were confirmed by $^{1}$H NMR. The signals around 10 ppm are related to protons from the amide group. It is well known, that mechanical and thermal properties of polyamides are directly related to their molecular weight. Higher molecular weights promote their properties. Therefore, molecular weight is needed to polymers. From the GPC data presented in Table 1. , it can be said that polyamides synthesized in this research have high molecular weight. Their thermal transitions and stability were determined using TGA, DSC and TMA, respectively. From TGA, DSC and TMA data of presented

in Table 1. .$T_s$ with the $\beta NH_2$ ratio increase is rising, $T_g$ was not observed in these polymers. It showed high transmittance for all polyamides.

Table 1. Characteristics of poly ($\beta$DATAMe-$\alpha$DATAMe-$\alpha$DACTA)

| $\beta$DATAMe/$\alpha$DATAMe | $T_{d10}$ [℃] | $T_g$ [℃] | $T_s$ [℃] | $M_n$ [g/mol] | $M_w$ [g/mol] | $M_w/M_n$ | Transmittance (450 nm)[%] |
|---|---|---|---|---|---|---|---|
| 25/75 | 339 | - | 112.5 | 38572 | 49312 | 1.28 | 92.2 |
| 50/50 | 336 | - | 112.4 | 36000 | 49071 | 1.36 | 94.2 |
| 75/25 | 359 | - | 131.3 | 36249 | 49086 | 1.35 | 94.6 |
| 100/0 | 328 | - | 223 | 462709 | 543224 | 1.17 | 93.6 |

3-2-2 Synthesis of poly{(4,4'-diyl-$\beta$-truxinic acid dimethyl ester) $\alpha$,$\omega$ alkyloylamide}

These alkyloylamide were prepared from **4** and carboxylic chloride as described in the Experimental section. The structures were confirmed by $^1$H NMR. The signals around 10 ppm are related to protons from the amide group. It is well known, that mechanical and thermal properties of polyamides are directly related to their molecular weight. Higher molecular weights promote their properties. Therefore, molecular weight is needed to polymers. From the GPC data presented in Table 2. , it can be said that polyamides synthesized in this research have high molecular weight. Their thermal transitions and stability were determined using TGA, DSC and TMA, respectively. From TGA, DSC and TMA data of presented in Table 2. . It shows a plot of $T_g$ of poly{(4, 4'-diyl-$\beta$ -truxinic acid dimethyl ester) $\alpha$, $\omega$ alkyloylamide} versus the carbon number in alkylenes(Figure 2), it is clear that $T_g$ of the novel renewable polyamides is directly related to the content of the length of alkyl chain. $T_g$ decreases with increasing number of carbon atoms in the aliphatic chain, it showed even-odd effect. It showed high transmittance for all polyamides.

Table 2. Characteristics of poly {(4,4'-diyl-$\beta$-truxinic acid dimethyl ester) α,ω alkyloylamide}.

| C | $T_{d10}$ [℃] | $T_g$ [℃] | $T_s$ [℃] | $M_n$ [g/mol] | $M_w$ [g/mol] | $M_w/M_n$ | Transmittance (450 nm)[%] |
|---|---|---|---|---|---|---|---|
| 5 | 331 | 158.1 | 128.4 | $4.2 \times 10^4$ | $1.0 \times 10^5$ | 2.37 | 91.5 |
| 6 | 351 | 93.7 | 125.5 | $4.2 \times 10^4$ | $9.4 \times 10^4$ | 2.24 | 95.6 |
| 7 | 340 | 126.2 | 124.4 | $4.2 \times 10^4$ | $1.1 \times 10^5$ | 2.57 | 98.8 |
| 8 | 352 | 92.2 | 104.8 | $3.6 \times 10^4$ | $4.4 \times 10^4$ | 1.24 | 94.9 |
| 9 | 345 | 80.6 | 105.6 | $3.8 \times 10^4$ | $4.9 \times 10^4$ | 1.28 | 97.4 |
| 10 | 353 | 79.3 | 120.8 | $4.0 \times 10^4$ | $5.3 \times 10^4$ | 1.34 | 97.2 |

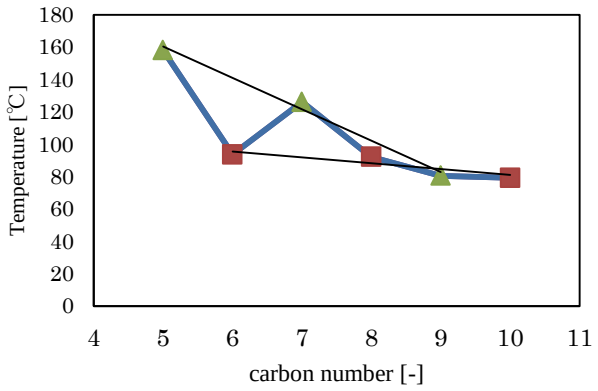



Figure 2. Plots of $T_g$ of poly{(4,4'-diyl-$\beta$-truxinic acid dimethyl ester) $\alpha,\omega$ alkyloylamide} versus the carbon number in alkylenes

**4. Conclusions**

I found that 4- aminocinnamic acid converted *syn* H-H type dimer, and the dimer was novel aromatic diamine. Furthermore novel bio-based aromatic-aromatic polyamides and aliphatic-aromatic polyamides were successfully synthesized from , 4,4'-diamino-$\beta$-truxinic acid dimethyl ester, 4,4'-diacetamide-$\alpha$-truxillic acid, 4'-diamino-$\alpha$-truxinic acid dimethyl ester and carboxylic dichloride. The data that these aromatic polyamides of thermal properties were changed with 4,4'-diamino-$\beta$-truxinic acid dimethyl ester ratio, and all polyamide have high transmittance . Finally aliphatic polyamides show $T_g$ decreases with increasing number of carbon atoms in the aliphatic chain, it showed even-odd effect. In addition it showed high transmittance for all polyamides.