공학석사학위논문

Synthetic Approach to Produce Poly(ester-amide)s Using Bio-based Diols

바이오 기반 다이올을 이용한
폴리에스터아마이드 수지 개발

2019 년 2 월

서울대학교 대학원

재료공학부

김 형 준

Abstract

Synthetic Approach to Produce Poly(ester-amide)s Using Bio-based Diols

Hyung Jun Kim

Department of Materials Science and Engineering

College of Engineering

Seoul National University

The growing interest in renewable resource-based feedstock chemicals and polymeric materials has promoted numerous studies in bio-sources. According to the current global production of bioplastics in 2017, PET and polyamide are the top two engineering plastics worldwide. PET exhibits disadvantages due to relatively low physical strength and T_g. One way to modify PET to yield a higher T_g and better mechanical properties is to combine polyesters and polyamides. Poly(ester-amide)s (PEAs) have a good

melt processability and a less water absorption known as a serious drawback of polyamide. For these reasons, PEAs are attracting widespread interests in many researchers. Though much effort has been involved into PEAs, most of the existing studies have increased biodegradability by polymerizing aliphatic PEAs and to the best of our knowledge, only a few studies have been conducted on PEAs for engineering plastics containing aromatic residues. In this study, for the development of bioplastics having mechanical properties superior to PET, monomers for the polymerization of PEAs were selected and synthesized based on amino acids and dimethyl esters which are non-edible bio-based materials. In the initial stage of the research, polymerization was attempted by synthesizing monomers of terephthalamide structure in order to have better mechanical properties. Monomers of terephthalamide structure had a high melting point due to excellent packing between the benzene ring and hydrogen bonding due to the presence of adjacent amide bonds. By this reason, monomers were decomposed when the polymerization proceeded at the melt-process, which made monomers of terephthalamide structure not suitable as monomers for thermal bulk polymerization. To overcome this problem, the amide bond was introduced into the aliphatic diol to lower the melting point and dimethyl terephthalate having a low melting point was selected as the

counterpart of polymerization that led to drastically lowering the melt-process temperature for thermal bulk polymerization. The thermal stability of every monomer and oligo-polymer synthesized by solution polymerization was evaluated. Four different diols were selected for thermal bulk polymerization based on the sufficient difference in their melting points and decomposition temperatures. In the same process as PET, thermal polymerization was successfully completed for all four diols and analyses were conducted by selecting the representative polymer synthesized with PSuP diol and DMT. Through FT-IR spectroscopy, it was confirmed that the polymer had both an ester bond and an amide bond. The model polymer having a weight average molecular weight of about 55,000 and a polydispersity index of 1.28 was polymerized. Thermal analysis showed that the glass transition temperature was nearly twice as high as that of PET, which enabled various fields to utilize PEAs in applications requiring much wider temperature range. Based on the results, the establishment of further experimental direction on how to change the internal carbon chain length of the diol will proceed.

Keywords: Bioplastics, Poly(ester-amide)s, Engineering Plastics, Thermal Bulk Polymerization, Polymerization with Bio-based materials

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1. INTRODUCTION

In recent years, polymers are pervasive throughout widespread fields such as food packaging, clothes, shelter, communication, transportation, construction, health care, and leisure industries.[1],[2] However, most of the polymers currently produced are based on petrochemistry feedstocks. Therefore, the growing interest in renewable resource-based feedstock chemicals and polymeric materials has promoted numerous studies on bio sources.[3],[4],[5] Recently, related studies tend to be overly biased towards lignin and 2,5-furandicarboxylic acid (FDCA).[6-11] The urge to find new bio-based molecules and to synthesize bioplastics has led to this study.

According to the current global production of bioplastics in 2017, PET and polyamide are among the top two engineering plastics worldwide. Especially, PET is one of the most important polymers known, with the annual total production being 6.7 million tons because of its cost, durability, and transparency.[12] However, relatively low T_g and physical strength of PET rigorously restrict the increase of the range of PET uses in some fields in which both good mechanical and heat-resistant properties are required. [13],[14] One way to modify PET in a way that yields a higher T_g and better mechanical properties is to combine polyesters and polyamides called

poly(ester-amide)s (PEAs) which also have a good melt processability and a less water absorption known as a serious drawback of polyamide.[15].[16] For these reasons, PEAs are attracting widespread interest in many researchers; for example, C. Girad and P. Garg synthesized PEAs based on various amino-alcohol and diamine. ε-caprolactone and ε-caprolactam were used as a reactant of ring opening reaction for synthesis of amino-alcohol, diamine, and diacid type monomers and copolymerization proceeded with butanediol. [17],[18]

Though much effort has been involved into PEAs, however, there are few precise ways to synthesize PEAs with an appropriate component and proper materials. Most of the existing studies have increased biodegradability of PEAs by polymerizing aliphatic PEAs and to the best of our knowledge, only a few studies have been conducted on PEAs for engineering plastics containing aromatic residues. Until now, these studies have only significances for the success of polymerization. [19-24]

The objectives of this study are to determine bio-based molecules and synthesis of monomers and polymerization of PEAs for engineering plastics which has satisfactory mechanical properties superior to PET. On the basis of these aims, three of non-edible amino acids were selected and monomers which had a terephthalamide structure were synthesized in the initial stage

of research. However, the thermal bulk polymerization with these monomers failed because of the high melting point caused by the terephthalamide structure. To overcome this problem, aliphatic diol monomers containing amide bonds were designed using some materials, such as dimethyl malonate and succinate, of the top 30 bio-based molecules selected by the department of energy, US. The tailor-made diols and DMT were used as monomers of PEAs and PEAs were polymerized successfully with 4 different diols.

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2. EXPERIMENTS

2.1 Materials

Dimethyl terephthalate (DMT, 99.0 %) was obtained from Acros Organics. (New Jersey, USA) Ethanolamine (> 98.0 %), dimethyl malonate (98.0 %), dimethyl adipate (> 99.0 %), terephthaloyl chloride (TCL, > 99.0 %), lithium methoxide (98.0 %), N,N-dimethyl acetamide (DMAc, 99.8 %, anhydrous), N,N-dimethyl formamide (DMF, 99.8 %, anhydrous), trimethylamine (TEA, > 99.0 %, anhydrous) and manganese (II) acetate (> 99.0 %) were purchased from Sigma-Aldrich (St. Louise, USA). Tyramine (> 98.0 %), 3-amino-1-propanol (> 99.0 %), dimethyl succinate (> 98.0 %), and dimethyl suberate (> 99.0 %) were obtained from Tokyo Chemical Industry (TCI, Tokyo, Japan). Cadaverine (99.9 %), ethylene glycol (99.0 %), titanium butoxide (99.0 %), and antimony triglycolate (99.9 %) were kindly received from Hyosung Co. Ltd (Anyang, Korea). Acetic anhydride (> 98.0 %), methanol (MeOH, 99.0 %), potassium hydroxide (KOH, 85.0 %), thionyl chloride ($SOCl_2$, 99.0 %), and dichloroethane (99.0 %) were purchased from Daejung Chemicals (Siheung, Korea). 2-Bromoethanol was obtained from Alfa-Aesar (Haverhill, USA). Dichloro-ethane was dried over calcium hydride before use and all the other reagents

were used as received without further purification.

2.2 Synthesis of Monomers with Terephthalamide Structure

2.2.1 Ethanolamine-DMT-Ethanolamine (EDE) Trimer

Ethanolamine (103.8 g, 1.7 mol) and DMT (50.0 g, 257.5 mmol) were added into a 250 mL 2-neck round bottom flask. The reaction was continued at 120 °C over 16 h under N_2 atmosphere equipped with a magnetic stirrer and a condenser. After the reaction, the reaction mixture was cooled enough at the room temperature and ethanol was added to the reaction mixture to remove a residual ethanolamine. The solution was filtered out and the precipitate was washed with diethyl ether at least two times to yield a white powder (Yield: 90 %). The product was dried at 50 °C vacuum oven until further use.

^{1}H-NMR (DMSO-d6, δ, ppm): 8.54 (2H, -OCN**H**-), 7.92 (4H, *Ar*H), 4.72 (2H, -CH$_2$O**H**), 3.54-3.31 (8H, -OCNHC**H$_2$**C**H$_2$**OH-)

2.2.2 Propanolamine-DMT-Propanolamine (PDP) Trimer

3-Amino-1-propanol (127.4 g, 1.7 mol) and DMT (50.0 g, 257.5 mmol) were added into a 250 mL 2-neck round bottom flask. PDP trimer was

prepared using the same synthetic procedure as the EDE trimer mentioned above. (Yield: 90 %)

^{1}H-NMR (DMSO-d6, δ, ppm): 8.55 (2H, -OCN**H**-), 7.89 (4H, *Ar*H), 4.49 (2H, -CH$_2$O**H**), 3.46-3.34 (8H, -OCNHC**H$_2$**CH$_2$**CH$_2$**OH), 1.72-1.68 (4H, -OCNHCH$_2$C**H$_2$**CH$_2$OH)

2.2.3 DMT-Cadaverine-DMT (DCD) X-mer

DMT (250.0 g, 1287.4 mmol) was dissolved in 1000 ml toluene and 50 ml methanol at 65 °C over 1 h, the boiling point of methanol, in a 2 L 3-neck round bottom flask equipped with a temperature sensor, an overhead mechanical stirrer, and nitrogen inlet condenser. When the DMT was completely dissolved in the solution, diluted cadaverine solution (32.9 g, 312.9 mmol in 80 ml of toluene) and LiOCH$_3$ catalyst solution (2.5 M LiOCH$_3$ in 30 ml of methanol) were added dropwise in the reaction mixture over 1 h. After dropwising entire solution, the nitrogen inlet was stopped and the temperature was gradually increased to 90 °C to distill off the methanol. The reaction was continued until the total reaction time was 24 h. As the reaction proceeded, the white precipitate was produced and after the total reaction time, the precipitate was filtered. The obtained product was washed two times with hot toluene and three times with methanol to remove

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remained reactants. (Yield: 80 %) The white powder of DCD X-mer was obtained and it was mixed from trimer to pentamer.

^{1}H-NMR (DMSO-d6, δ, ppm): 8.65 (2H, -OCN**H**-), 7.90-8.08 (8H, *Ar*H), 3.88 (6H, -COOC**H₃**), 3.30 (4H, -OCNHC**H₂**CH₂-), 1.35-1.59 (6H, -NHCH₂**CH₂CH₂CH₂**CH₂NH-)

2.2.4 MCCB-Cadaverine-MCCB (MCM) Trimer

In order to overcome the failure of the molecular weight control in case of DCD X-mer, the reaction proceeded with a new scheme. The MCM trimer was synthesized through 3 steps. First, DMT (70.0 g, 360.5 mmol) and KOH (18.2 g, 324.4 mmol) were dissolved in 700 ml methanol in a 1 L 2-neck round bottom flask. The reaction mixture was heated to reflux over 3.5 h. After the reaction, the solvent was removed under reduced pressure in a rotary evaporator and the white solid was obtained. The obtained white solid was then dissolved in distilled water and filtered out a precipitate, remained DMT. The filtered solution was acidified with concentrated HCl to low pH until a white solid precipitated out. The precipitate was then washed with water several times upon which it became neutral. (Yield: 81 %) This white solid was called monomethyl terephthalate (MMT).

^{1}H-NMR (DMSO-d6, δ, ppm): 13.35 (1H, -COO**H**), 8.06 (4H, *Ar*H),

3.88 (3H, -COOC**H₃**)

MMT (5 g, 27.8 mmol) was added into 50 ml dichloroethane in a 100 mL 2-neck round bottom flask equipped with a nitrogen inlet condenser. Thionyl chloride (16.5 g, 138.8 mmol) was also added into the reaction mixture and was heated to 80 °C over 3.5 h. It was indirectly known that the reaction proceeded through the dissolution of the undissolved MMT. After the reaction, the solvent was removed under reduced pressure in a rotary evaporator and the slightly brown solid was obtained (Methyl 4-(chlorocarbonyl) benzoate, MCCB). The last step proceeded *in situ* with this product.

MCCB (3 g, 15.9 mmol), cadaverine (0.8 g, 8.0 mmol) and TEA (2.4 g, 23.9 mmol) were dissolved in 60 ml of DMAc in a 100 mL 2-neck round bottom flask. The reaction was continued at the room temperature over 12 h under N_2 atmosphere. After the reaction, the reaction mixture was poured into 10-fold distilled water and the white solid precipitated out. The precipitate was washed three times with distilled water and kept at 50 °C vacuum oven until further use. (Yield: 90 %)

^{1}H-NMR (DMSO-d6, δ, ppm): 8.62 (2H, -CON**H**-), 7.91-8.01 (8H, *Ar*H), 3.87 (6H, -COOC**H₃**), 3.26 (4H, -OCNHC**H₂**CH₂-), 1.35-1.59 (6H, -

NHCH$_2$**CH$_2$CH$_2$CH$_2$**CH$_2$NH-)

2.2.5 Tyramine-TCL-Tyramine (TTT) Trimer

Tyramine (50.0 g, 364.5 mmol) and TEA (18.4 g, 182.2 mmol) were dissolved in 500 ml of DMF in 1 L 2-neck round bottom flask. When the tyramine was entirely dissolved in DMF, TCL solution (24.6 g, 121.5 mmol in 150 ml of DMF) was added dropwise in the reaction mixture. The reaction was continued at the room temperature over 12 h under N$_2$ atmosphere. After the reaction, the reaction mixture was dissolved in 1 M NaOH solution and filtered out. The filtered solution was then acidified with conc. HCl to pH 1 upon which a white solid precipitated out. The precipitate was washed with water at least three times to neutralize acidity. (Yield: 85 %)

^{1}H-NMR (DMSO-d6, δ, ppm): 9.17 (2H, -*Ar*O**H**), 8.62 (2H, -CON**H**-), 7.87 (4H, -NHCO*Ar***H**CONH-), 6.66-7.03 (8H, HO*Ar***H**CH$_2$-), 3.41 (4H, -CONHC**H$_2$**CH$_2$-), 2.72 (4H, HO*Ar*HC**H$_2$**CH$_2$-)

2.2.6 Ethanol-Tyramine-TCL-Tyramine-Ethanol (ETTTE) Pentamer

TTT trimer (2.0 g, 4.9 mmol), and K$_2$CO$_3$ (2.7 g, 14.8 mmol) were dissolved in 40 ml of ethanol in 100 mL 2-neck round bottom flask

equipped with a nitrogen inlet condenser. The reaction mixture was heated to reflux over 3 h to activate terminal OH group of TTT trimer. 2-Bromoethanol (1.9 g, 14.8 mmol) was then added dropwise in the reaction mixture and the reaction was continued over 24 h. When the reaction was finished, the reaction mixture was poured into 1 M NaOH solution and the slightly brown solid precipitated out. The precipitate was washed plenarily with water and kept at 50 °C vacuum oven until further use. (Yield: 80 %)

^{1}H-NMR (300MHz; DMSO-d6): δ (ppm) 8.63 (2H, -CON**H**-), 7.87 (4H, -NHCO*Ar***H**CONH-), 6.84-7.16 (8H, -CH$_2$O*Ar***H**CH$_2$-), 4.83 (2H, -CH$_2$O**H**) 3.92 (4H, -CH$_2$*Ar*OC**H$_2$**-), 3.70 (4H, -*Ar*OCH$_2$C**H$_2$**OH), 3.46 (4H, CONHC**H$_2$**CH$_2$-), 2.78 (4H, -O*Ar*HC**H$_2$**CH$_2$-)
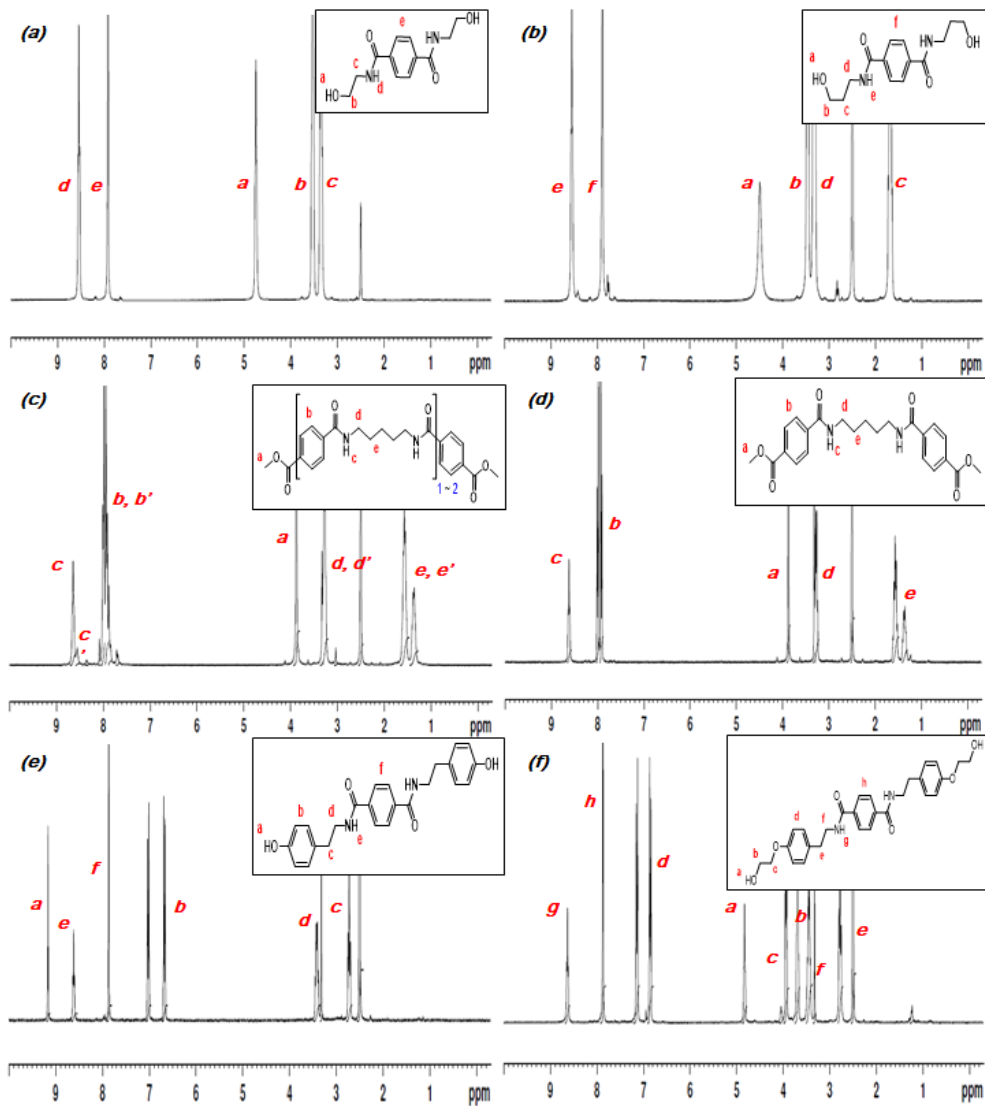
Figure 1. ^{1}H-NMR Spectra of (a) EDE trimer, (b) PDP trimer, (c) DCD X-mer, (d) MCM trimer, (e) TTT trimer, and (f) ETTTE pentamer

2.3 Synthesis of Aliphatic Diol Monomers Containing Amide Bonds

2.3.1 Dimethyl Malonate Based Diol (EME/PMP)

Dimethyl malonate (10.0 g, 75.7 mmol), and ethanolamine (30.5 g, 499.5 mmol) / 3-amino-1-propanol (37.5 g, 499.5 mmol) were added into a 100 mL 2-neck round bottom flask equipped with a nitrogen inlet condenser. The reaction was continued at 120 ℃ over 16 h. After the reaction, the reaction mixture was dissolved in 300 ml of DMF and poured slowly into 1500 ml of diethyl ether. The white solid precipitated out and filtering the ether solution to collect the precipitate proceeded. The above procedure was repeated twice and pure white powder was obtained. (Yield: 95%) The product was kept at 50 ℃ vacuum oven until further use.

^{1}H-NMR (DMSO-d6, δ, ppm, EME diol): 8.01 (2H, -CON**H**-), 4.67 (2H, -CH$_2$O**H**), 3.40 (4H, -C**H$_2$**OH), 3.15 (4H, -CONHC**H$_2$**CH$_2$OH), 3.03 (2H, -NHCOC**H$_2$**CONH-)

^{1}H-NMR (DMSO-d6, δ, ppm, PMP diol): 7.94 (2H, -CON**H**-), 4.42 (2H, -CH$_2$O**H**), 3.40 (4H, -C**H$_2$**OH), 3.13 (4H, -CONHC**H$_2$**CH$_2$-), 3.03 (2H, -NHCOC**H$_2$**CONH-) 1.50-1.58 (4H, -CONHCH$_2$C**H$_2$**CH$_2$OH)

2.3.2 Dimethyl Succinate Based Diol (ESE/PSP)

Dimethyl succinate (10.0 g, 68.4 mmol), and ethanolamine (27.58 g, 451.6 mmol) / 3-amino-1-propanol (33.92 g, 451.6 mmol) were added into a 100 mL 2-neck round bottom flask equipped with a nitrogen inlet condenser. The synthetic procedure of ESE/PSP diol was exactly same as EME/PMP diol.

^{1}H-NMR (DMSO-d6, δ, ppm, ESE diol): 7.79 (2H, -CON**H**-), 4.61 (2H, -CH$_2$O**H**), 3.35 (4H, -C**H$_2$**OH), 3.10 (4H, -CONHC**H$_2$**CH$_2$OH), 2.28 (4H, -NHCOC**H$_2$**C**H$_2$**CONH-)

^{1}H-NMR (DMSO-d6, δ, ppm, PSP diol): 7.76 (2H, -CON**H**-), 4.39 (2H, -CH$_2$O**H**), 3.38 (4H, -C**H$_2$**OH), 3.07 (4H, -CONHC**H$_2$**CH$_2$-), 2.27 (4H, -NHCOC**H$_2$**C**H$_2$**CONH-) 1.47-1.56 (4H, -CONHCH$_2$C**H$_2$**CH$_2$OH)

2.3.3 Dimethyl Adipate Based Diol (EAE/PAP)

Dimethyl adipate (10.0 g, 57.4 mmol), and ethanolamine (23.1 g, 378.9 mmol) / 3-amino-1-propanol (28.5 g, 378.9 mmol) were added into a 100 mL 2-neck round bottom flask equipped with a nitrogen inlet condenser. The synthetic procedure of EAE/PAP diol was exactly same as the other diols.

^{1}H-NMR (DMSO-d6, δ, ppm, EAE diol) : 7.74 (2H, -CON**H**-), 4.63 (2H, -CH$_2$O**H**), 3.37 (4H, -C**H$_2$**OH), 3.10 (4H, -CONHC**H$_2$**CH$_2$OH), 2.03 (4H, -NHCOC**H$_2$**CH$_2$CH$_2$C**H$_2$**CONH-), 1.47-1.56 (4H, -NHCOCH$_2$C**H$_2$**C**H$_2$**CH$_2$-CONH-)

^{1}H-NMR (DMSO-d6, δ, ppm, PAP diol): 7.72 (2H, -CON**H**-), 4.40 (2H, -CH$_2$O**H**), 3.37 (4H, -C**H$_2$**OH), 3.10 (4H, -CONHC**H$_2$**CH$_2$-),   2.03 (4H, -NHCOC**H$_2$**CH$_2$CH$_2$C**H$_2$**CONH-), 1.43-1.56 (8H, -NHCOCH$_2$C**H$_2$**C**H$_2$**CH$_2$-CONH- / -CONHCH$_2$C**H$_2$**CH$_2$OH [Overlapped])

2.3.4 Dimethyl Suberate Based Diol (ESuE/PSuP)

Dimethyl suberate (10.0 g, 49.4 mmol), and ethanolamine (19.9 g, 326.3 mmol) / 3-amino-1-propanol (24.51 g, 326.3 mmol) were added into a 100 mL 2-neck round bottom flask equipped with a nitrogen inlet condenser. The synthetic procedure of EAE/PAP diol was exactly same as the other diols.

^{1}H-NMR (DMSO-d6, δ, ppm, ESuE diol): 7.73 (2H, -CON**H**-), 4.61 (2H, -CH$_2$O**H**), 3.36 (4H, -C**H$_2$**OH), 3.10 (4H, -CONHC**H$_2$**CH$_2$OH), 2.01-2.27 (4H, -NHCOC**H$_2$**-), 1.45 (4H, -NHCOCH$_2$C**H$_2$**CH$_2$-), 1.21 (4H, -NHCO-CH$_2$CH$_2$C**H$_2$**C**H$_2$**CH$_2$CH$_2$CONH-)

^{1}H-NMR (DMSO-d6, δ, ppm, PSuP diol): 7.71 (2H, -CON**H**-), 4.40 (2H, -CH$_2$O**H**), 3.37 (4H, -C**H$_2$**OH), 3.07 (4H, -CONHC**H$_2$**CH$_2$-), 2.02 (4H, -NHCOC**H$_2$**-) 1.43-1.56 (4H, -CONHCH$_2$C**H$_2$**CH$_2$- / -CONHCH$_2$C**H2**-CH2OH [Overlapped])
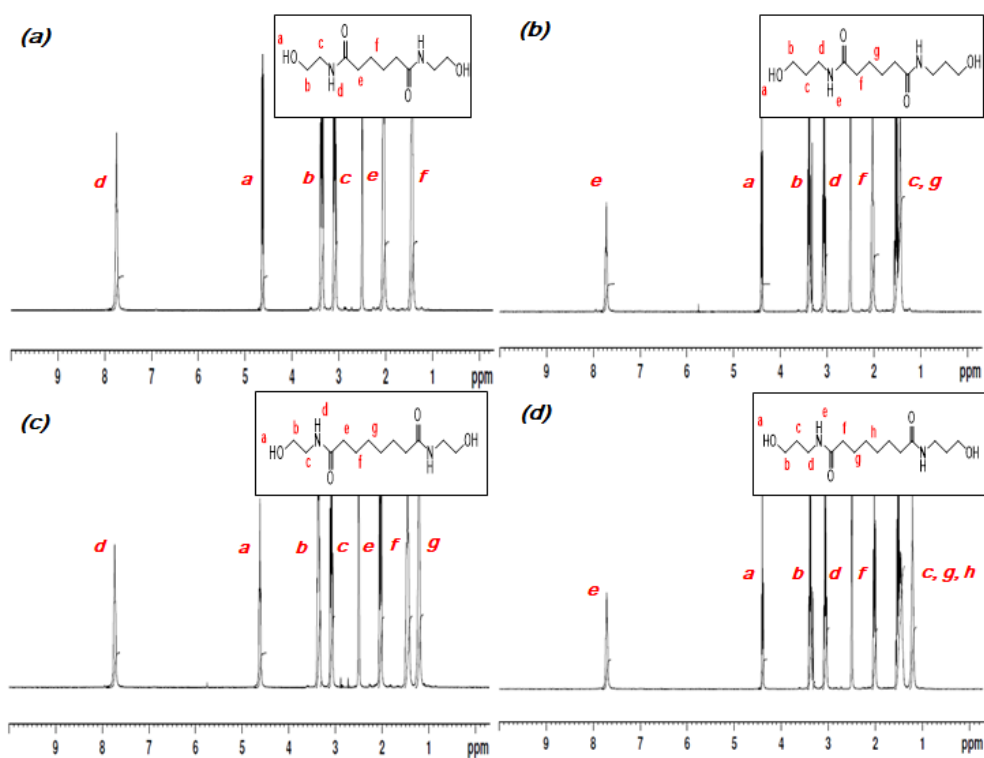
Figure 2. ^{1}H-NMR Spectra of diols used for thermal bulk polymerization;

(a) EAE diol, (b) PAP diol, (c) ESuE diol, and (d) PSuP diol

2.4 Solution Polymerization of Poly(ester-amide)s

2.4.1 Polymerization with Terephthalamide Structure Monomers

2.4.1.1 EDE Trimer

EDE trimer (10.0 g, 39.6 mmol) was dissolved in 150 ml of anhydrous DMF in 250 mL 2-neck round bottom flask. EDE trimer was dissolved sufficiently at the room temperature for 30 min with an intense nitrogen purging. TCL (8.0 g, 39.6 mmol) was then added into the reaction mixture with vigorous stirring. TEA (8.0 g, 79.3 mmol) was added at 30 min after the addition of TCL. After about 30 min from the addition of TEA, stirring was no longer possible and the reaction is terminated spontaneously. The pudding-like product was filtered by precipitation in excess water. The precipitate was washed two times with water and kept at 50 °C vacuum oven.

2.4.1.2 MCM Trimer

In order to proceed solution polymerization, the introduction of acyl chloride functional group at both ends of the MCM trimer was performed first.MCM trimer (3.0 g, 7.0 mmol), KOH (1.2 g, 21.1 mmol) were dissolved in 40 ml of methanol in a 100 mL 2-neck round bottom flask. The reaction mixture was heated to reflux over 3.5 h. After the reaction, the

solvent was removed with a rotary evaporator. The remaining solid was dissolved in distilled water and filtered out. The filtered solution was acidified with conc.HCl to low pH until the white solid precipitated out. The precipitate was washed several times with water. The product was called MCM-OH trimer and kept at 50 ℃ vacuum oven before use. MCM-OH trimer (3.0 g, 7.5 mmol) and thionyl chloride (4.5 g, 37.7 mmol) were dissolved in 40 ml of distilled dichloroethane in a 100 mL 2-neck round bottom flask equipped with a nitrogen inlet condenser. The reaction was continued at 80 ℃ over 3.5 h. It was indirectly known that the reaction was terminated through the dissolution of the undissolved MCM-OH trimer. After the reaction, rotary evaporating the solvent proceeded and the slightly brown solid was obtained. The product was called MCM-Cl trimer and it was used as a monomer of solution polymerization. EG (0.3 g, 5.0 mmol), and TEA (1.0 g, 10.0 mmol) were dissolved in 25 ml of DMF in a 100 mL 2-neck round bottom flask under N_2 atmosphere. MCM-Cl trimer (2.2 g, 5.0 mmol) was then added into the reaction mixture with vigorous stirring. The other procedure of solution polymerization was same as the EDE trimer.

2.4.1.3 TTT Trimer

TTT trimer (10.0 g, 24.7 mmol) was dissolved in 100 ml of anhydrous DMF in 250 mL 2-neck round bottom flask. The reaction temperature was raised to 50 °C since the TTT trimer was not well-soluble. TCL (5.0 g, 24.7 mmol) was added into the reaction mixture after enough dissolution of TTT trimer. The reaction was continued at the room temperature and TEA was added 30 min after the addition of TCL. The following procedure of solution polymerization was same as the EDE and MCM-Cl trimer.

2.4.2 Polymerization with Aliphatic Diol Monomers

The solution polymerization was carried out using a total of eight synthesized diols. The polymerization method proceeded in the same way for all of the diols. The reaction was conducted on the basis of 3.0 g of each diol, and the molar compositions of diol, TCL, TEA were set at 1:1:2. As a representative, EME diol (3.0 g, 15.8 mmol) was dissolved in 40 ml of DMF in a 100 mL 2-neck round bottom flask. After sufficiently dissolving the EME diol for 30 min with an intense N_2 purging, TCL (3.2 g, 15.8 mmol) was added into the reactor with vigorous stirring. TEA (3.2 g, 31.5 mmol)

was then added into the reactor after another 30 min. As the reaction progressed, the viscosity of the reaction mixture increased, and stirring became impossible in a short period of time. The reaction mixture then was placed in excess water and filtered out. The precipitate was washed several times to remove TEA and its salts.

2.5 Thermal Bulk Polymerization of Poly(ester-amide)s

The polymerization of poly(ester-amide)s (PEAs) proceeded in the same manner as the general PET polymerization. The polymerization process consisted of two successive steps; oligomerization (transesterification) and polycondensation. Similar to the PET polymerization method, manganese acetate was used as a catalyst for oligomerization (transesterification) and antimony oxide / triglycolate or titanium butoxide were used as a catalyst for polycondensation. For the second step, polycondensation, a vacuum condition which is about 1 torr was required.

2.5.1 Polymerization with Terephthalamide Structure Monomers

2.5.1.1 EDE/PDP Trimer, EG, DMT Terpolymer

The overall compositions of monomers were listed in table 1. Polymerization of terpolymer was performed with EG, EDE/PDP trimer, and DMT.

First of all, regular PET was polymerized for comparison of the feasibility of polymerization. EG (21.0 g, 338.3 mmol), DMT (31.28 g, 161.1 mmol), manganese acetate (15.7 mg, 300 ppm), and antimony oxide (20.9 mg, 400 ppm) were added into a 250 mL 2-neck round bottom flask equipped with an overhead mechanical stirrer. The reaction mixture was heated to 210 ℃ over 3.5 h with a beads condenser for fractional distillation of methanol. After the transesterification process, a beads condenser was removed and then the temperature was increased to 250 ℃ with vacuum condition. The reaction was continued over 3 h in vacuo. When the reaction was finished, the reaction mixture was poured on to a metal tray filled with water. The product was then kept at 25 ℃ vacuum oven until further use.

Secondly, EG, DMT, EDE trimer based terpolymers were polymerized. The two different compositions of terpolymer, (EG : EDE trimer : DMT) ;

(2.0 : 0.1 : 2.1), (1.6 : 0.5 : 2.1), were polymerized. EG (20.0 g, 322.2 mmol / 16.0 g, 257.8 mmol), EDE trimer (4.06 g, 16.1 mmol / 20.3 g, 80.6 mmol), DMT (31.28 g, 161.1 mmol), manganese acetate (16.6 mg / 20.3 mg, 300 ppm), and antimony oxide (22.1 mg / 27.0 mg, 400 ppm) were added into a 250 mL 2-neck round bottom flask. Both terpolymers were polymerized in the same procedure as the regular PET polymerization mentioned above.

Third, the polymerization with PDP trimer was carried out in the same compositions as in EDE trimer. EG (3.5 g, 57.0 mmol / 2.8 g , 45.7 mmol), PDP trimer (0.8 g, 2.9 mmol / 4.0 g, 14.3), DMT (5.54 g, 28.5 mmol), manganese acetate (2.9 mg / 3.7 mg, 300 ppm), and antimony oxide (3.9 mg / 4.9 mg, 400 ppm) were added into a 100 mL 2-neck round bottom flask. PDP based terpolymer was also polymerized in the same method as regular PET and EDE based terpolymer.

Table 1. Compositions, reaction conditions, and photo image of EDE/PDP trimer, EG, and DMT terpolymerization

No	Monomer molar ratio			Catalyst	Reaction time	Product State	Photo image
	HO-R-OH		HOOC-R-COOH				
	EG	EDE trimer	DMT				
1	1 (2.1)	-	1	Manganese acetate, antimony oxide	3.5 h / 3 h	White / polymer	
2	0.9 (2.0)	0.1	1			Brown / oligo-polymer	
3	0.5 (1.6)	0.5	1			Brown / Oligomer	

No	EG	PDP trimer	DMT	Catalyst	Reaction tiime	Result	Photo image
4	0.9 (2.0)	0.1	1	Maganese acetate, antimony oxide	3.5 h / 3 h	Soft brown / polymer	
5	0.5 (1.6)	0.5	1			Brown / oligo-polymer	

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2.5.1.2 DCD X-mer Based Poly(ester-amide)s

In the case of DCD X-mer, polymerization was performed with more various compositions in comparison with EDE/PDP based PEAs, and polymerization without using EG was carried out three times in total with different polymerization time as shown in Table 2. The detailed compositions of monomers and the scale of reactions were listed in Table 2. The weight scale of all the polymerizations was carried out on the basis of 200.0 g of DCD X-mer. As a representative, DCD X-mer (200 g, 400.0 mmol), EG (52.1 g, 840.0 mmol), manganese acetate (75.6 mg, 300 ppm), and antimony oxide (100.8 mg, 400 ppm) were added into a 1 L 3-neck separable reaction vessel equipped with an overhead mechanical stirrer, a temperature sensor, and a beads condenser. The junctions of glassware and joints were covered with a vacuum grease and a metal clamp to prevent external leakage of reactants and air. The reaction mixture was heated to 280 °C for the transesterification process. After 3.5 h, a beads condenser was removed and the reaction temperature was increased to 300 °C with an applying vacuum condition. The polycondensation was performed with changing the polymerization time to 4, 5, 6 h. After the polycondensation, the reaction mixture was collected carefully and kept at 50 °C vacuum oven until further use. All the other polymerizations with different compositions

were conducted in the same manner as mentioned above.

Table 2. Compositions, reaction conditions, and photo image
of DCD X-mer, and EG polymerization

No	Monomer molar ratio		Catalyst	Reaction time	Vacuum condition	Product state	Photo image
	HOOC-R-COOH	HO-R-OH					
	DCD X-mer	EG					
1	1	2.1		4 h	0.62 torr	Oligomer (Carbonization)	
2	1	2.1	Maganese acetate, antimony oxide	5 h	0.95 torr	Oligomer (Carbonization)	
3	1	2.1		6 h	0.92 torr	Oligomer (Carbonization)	

2.5.1.3 Acetylation of TTT Trimer for Polymerization of PEAs

TTT trimer (20.0 g, 49.5 mmol), acetic anhydride (6.1 g, 59.4 mmol), and potassium acetate (3mg, catalytic amount) were added into a 100 mL 2-neck round bottom flask equipped with a beads condenser. At the beginning of the reaction, the reaction mixture was heated to 140 ℃, the boiling point of acetic anhydride. The reaction temperature was gradually increased to 250 ℃ over 3.5 h. The reaction mixture was a heterogeneous phase because the melting point of TTT trimer was about 280 ℃. After the reaction, rotary evaporating the acetic acid was performed in 40 ℃ water bath and the product was kept at 50 ℃ vacuum oven.

2.5.2 Polymerization with Aliphatic Diol Monomers

Polymerization of PEAs was carried out by the same process as regular PET and using four diols, which were confirmed to be easy to set the process temperature through thermal analysis; EAE, PAP, ESuE, PSuP diol. In order to select the catalyst for the polycondensation process, a comparison reaction was carried out using an antimony catalyst and a titanium catalyst. EAE diol and PSuP diol were used as a comparison

reaction and reaction profile was listed on table x. Polymerizations to determine polymerizability were performed on a small scale, under the same conditions for all four diols. As a representative, EAE diol (10.0 g, 43.1 mmol), DMT (4.0 g, 20.5 mmol), manganese acetate (4.19 mg, 300 ppm), and titanium butoxide (16.7 mg, 2.4 mmol/mol DMT) or antimony triglycolate (17.1 mg, 2.4 mmol/mol DMT) were added into a 100 mL 2-neck round bottom flask equipped with an overhead mechanical stirrer and a beads condenser. The reaction vessel was placed in heat mantle with an internal temperature sensor. The reaction mixture was heated to 170 °C over 3.5 h for the oligomerization process. For the next step, polycondensation was performed subsequently and the reaction temperature was increased to 200 °C with an applying vacuum condition. As the reaction progressed, a stronger vacuum is applied up to about 1 torr, and the temperature was gradually raised to about 30 °C below the decomposition temperature of the polymer. The polycondensation reaction was stopped spontaneously as the impeller could not stir the mixture because of its high viscosity. The brown-colored polymer was obtained and kept at 50 °C vacuum oven until further use. Polymerizations with the other diols were conducted in the same method as the polymerization with EAE diol.

2.5.2.1 Large Scale Polymerization for Preparation of Tensile Test Specimen.

PSuP diol was selected as a model compound and large-scale polymerization was carried out for the evaluation of mechanical properties. PSuP diol (70.0 g, 242.7 mmol), DMT (22.5 g, 115.6 mmol), manganese acetate (27.7 mg, 300 ppm), and antimony triglycolate (96.1 mg, 2.4 mmol/mol DMT) were added into a tailor-made glassware for ejection to collect product easily. The reaction mixture was heated to 170 ℃ over 3.5 h and stirred at a speed of 60 rpm using a mechanical stirrer. After the oligomerization process, the reaction temperature was increased to 200 ℃ and applying a wear vacuum condition, about 100 torr, proceeded. The viscosity of the reaction mixture was checked through the torque value of the mechanical stirrer and the temperature was gradually raised to 290 ℃ and the vacuum is strongly applied. The byproducts generated during the reaction should be removed so as not to block the joints, and the reaction should proceed effectively to maintain the vacuum condition inside the reactor. When the viscosity of the reaction mixture reached to 30 Ncm, which is the limit of nitrogen ejection of the used reactor, the reaction was stopped and nitrogen was injected into the reactor and the product was ejected underneath. Nitrogen ejection was carried out carefully on a metal

tray containing water, allowing the product to be cooled immediately. The obtained polymer was kept at 50 °C vacuum oven until further use.

2.6 Characterization

^{1}H-NMR spectra were recorded on a Bruker AVANCE-300, FT-NMR spectrometer, using 5 mm QNP, 5 mm Dual, 10 mm Dual as a probe. Dimethyl sulfoxide-d6 (99.96 atom % D, Sigma-Aldrich) was used as the solvent for all of the chemical compounds. Unfortunately, polymerization products were not dissolved in any solvents available for analysis equipment mentioned above. The concentration of each sample was the same as 10 mg/ml and the scan number of every sample was equally 16.

The molecular weight of PEAs was measured by an Agilent 1200 GPC system equipped with waters styragel HR 5E+HR 4E column and UV detector. The used eluent was hexafluoroisopropanol (HFIP)/chloroform: 2/98 (v/v). The sample (0.0105 g) was dissolved in 0.2 ml of HFIP and 0.5 ml of chloroform with using sonication. 0.1 volume % of this solution was taken and diluted in 1.4 ml of chloroform containing 0.01 v % anisole. This solution was used as the sample of GPC.

FT-IR spectra were measured by a Bruker Tensor 27, FT-IR spectrometer. The measured wavelength range was from 400 to 4000 cm^{-1}, and the resolution was 4 cm^{-1}. The scan number for each sample was 32, and the sample used for the analysis was used without further treatment.

2.7 Thermal Properties

Thermal properties were characterized by three different instruments. First, differential scanning calorimetry (DSC) was carried out using a TA instrument Q-10. All measurements were performed under N_2 atmosphere and approximately 10 mg of each sample was loaded hermetically in the standard aluminum pan. Both heating and cooling rate of the instrument were configured as a 10 °C/min.

Secondly, Thermo-gravimetric analysis (TGA) was conducted by TA instrument Q-50 under a nitrogen atmosphere. Each sample was heated to 110 °C in advance to remove residual moisture. The weight-loss curve and its derivative values were obtained in the range of 30 °C-600 °C at a rate of 10 °C/min.

Third, the melting point which could not be defined by DSC analysis was determined by using melting point analyzer, Bibby Sterlin SMP 10. The

sample powder was placed in a 2 mm diameter capillary tube and heated in a small furnace which had a narrow visible hole in its top. The melting point of all samples was visually confirmed.

2.8 Mechanical Properties

The specimens for the tensile test were prepared with using a BABYPLAST injection molding machine, according to ISO 527-2, dumbbell-shaped specimens (1 BB type; 2 mm in thickness and 2 mm in width).

Experiment in progress

3. RESULTS AND DISCUSSION

3.1 Synthesis of Monomers and Polymerization with Terephthalamide

In the early stage of the research, this study tried to synthesize monomer of terephthalamide structure with amide bonds next to the benzene ring in order to increase the proportion of aromatic rings in the molecular structure to increase the mechanical properties. Three amino acids, Serine, Lysine, and Tyrosine, were selected from bio-based materials with amine functional groups, and monomers were synthesized by using these amino acids derivatives; Ethanolamine, Cadaverine, Tyramine, which was conducted the decarboxylation reaction.[25] With the aim of polymerizing in the same process as PET, the terephthalic diacid and EG, which are the monomers of PET, were fixed in the counterpart of monomer synthesis or polymerization at the beginning of the research. Based on the above three bio-based compounds, a total of five types of X-mer synthesis were performed and it was confirmed that the synthesis was successfully carried out by NMR analysis. Among five compounds, EDE trimer and DCD X-mer were used for thermal bulk polymerization and EDE trimer, MCM trimer, and TTT trimer were used for solution polymerization.

First, the thermal bulk polymerization with EDE trimer was carried out

by using EDE trimer and EG as diol and DMT as diacid. The molar ratios of EDE trimer and EG were varied in three different ways; 0/2.1, 0.1/2.0, 0.5/1.6. As the molar ratio of EDE trimer was increased, the degree of discoloration was increased and the degree of polymerization was decreased. The degree of polymerization was evaluated by the viscosity of the polymer at the end of the polymerization. The decrease in the degree of polymerization with increasing molar ratio of EDE trimer might be due to the short carbon chain length from the terephthalamide structure to the terminal OH group. Based on the above assumption, Synthesis of the PDP trimer which had a longer carbon chain than the EDE trimer proceeded and the thermal bulk polymerization was performed under the same conditions as the EDE trimer. As a result of the comparative analysis of thermal polymerization products, it was confirmed that the degree of polymerization using PDP trimer was higher than that of EDE trimer. However, when the molar ratio of PDP trimer was increased, the degree of polymerization was low similarly to EDE trimer.

Second, the DCD X-mer was thermally polymerized in various compositions as shown in table 2. Similar to EDE trimer, the degree of polymerization was found to decrease with increasing molar ratio of DCD X-mer. In order to increase the degree of polymerizations, the reaction time

was increased from 4 h to 6 h. However, all of the results were obtained at low molecular weight, oligomer, and severe discoloration and brittleness due to carbonization were observed. For the better polymerization, a new synthesis of monomer, MCM trimer, which could control the molecular weight accurately without using a catalyst proceeded.

Third, in the case of TTT trimer, the reactivity of the terminal functional group was low because both ends were phenol, and two methods were used to improve its reactivity. One was acetylation of both ends of the TTT trimer *in situ* prior to polymerization to improve the reactivity and proceeded the polymerization continuously.[26] However, since the boiling point of acetic anhydride, which was a reagent used in the acetylation reaction, was 140 ℃ and the melting of the TTT trimer was 280 ℃, the TTT trimer remained in a solid state at a reaction temperature of about 140 ℃. The reaction temperature was raised to 250 ℃, however, the TTT trimer still was not melted. By this reason, the reaction had to proceed unavoidably in a heterogeneous phase state. In order to confirm whether the reaction proceeded successfully under these conditions, the NMR analysis was conducted after the reaction, and it was judged that it was not suitable to proceed with this method because of no differences in NMR spectra. The other method was to synthesize pentamer with enhanced reactivity by

conjugating bromoethanol to the OH group at the end of the TTT trimer. After successfully activating the terminal functional group of TTT trimer with K_2CO_3, it succeeded in conjugating ethanol, however, the thermal bulk polymerization did not proceed because the melting point of pentamer was too high.

The solution polymerization was carried out in order to indirectly confirm the properties of the polymer before thermal bulk polymerization because it was easy to conduct experiments with a relatively small scale as compared with thermal bulk polymerization and the process was simple. After observing the phenomenon of carbonization during the thermal bulk polymerization, the thermal properties of the compounds such as the melting point and the decomposition temperature were important factors for the feasibility of thermal bulk polymerization. For these reasons, the oligo-polymer was polymerized through solution polymerization and the thermal analysis thereof was carried out. The EDE, MCM, and TTT trimer were used for the solution polymerization and the high molecular weight polymer was not obtained due to the limitation of the solubility in the solvent. GPC and NMR could not be analyzed because of insolubility in usable solvents. Only the melting point and decomposition temperature were measured through thermal analysis.

3.2 Analyses of Causes of Failure in Thermal Bulk Polymerization and Establishment of New Experimental Direction.

When the polymerization was carried out with compounds having a terephthalamide structure, all of the polymerizations was failed and the carbonization occurred in every polymerization. The leading cause of failure in thermal bulk polymerization was the failure to set the process temperature. This was confirmed by several analyses, especially TGA. Figure 3 was a collection of TGA thermograms of the compounds used in the polymerization. The isothermal state was maintained for 1 h under N_2 atmosphere at the temperature at which the polymerization proceeded, and it was confirmed that the decomposition occurred at each process temperature. In order to better confirm the decomposition behavior of these compounds at the process temperature, compounds were placed between cover glasses in the hot-stage and allowed to stand at the process temperature for the process time, resulting in discoloration and carbonization. The NMR spectrum of these compounds confirmed that the decomposition of terephthalamide occurred, and the ninhydrin test was also carried out to verify the decomposition of the amide bond next to the benzene ring. The result of the ninhydrin test was positive, therefore this meant decomposition of the amide bond, which was the most important reason for the failure of

polymerization and the occurrence of carbonization. If the oligomerization reaction occurred and the decomposition temperature of the reaction compounds was increased, it was considered that polymerization might be possible due to no decomposition. For this reason, thermal analysis of the oligo-polymer polymerized through solution polymerization was conducted as shown in Figure 4. As a result of TGA under the same conditions as the compound used in the polymerization, it was confirmed that the decomposition proceeded similar to the compound used in the solution polymerization, and it was judged that thermal bulk polymerization using the synthesized, 'terephthalamide structure' compound would be difficult. In the case of terephthalamide, the melting point was very high because of the dense-packing between the aromatic rings and the strong hydrogen bonding due to amide bonds. The decomposition temperature of the amide bond in terephthalamide structure was also about 300 ℃, therefore it was almost impossible to set the process temperature of the thermal bulk polymerization proceeding at the melt phase.

In order to facilitate successful thermal bulk polymerization which was easy to apply in industry, the process temperature setting which required a sufficient difference between the melting point and the decomposition temperature was important. When the terephthalamide structure was

continuously used, the length of the carbon chain from the benzene ring should be extended to lower the melting point. However, because the limit was existed to finding bio-based molecules suitable for use. In addition, the polymerization counterpart of diacid was fixed with EG, and it was known that EG also decomposed about 300 °C.[27] Therefore, a new research direction was established to set a low process temperature. The most important part for a new research direction was that the melting point should be sufficiently different from the decomposition temperature to conduct thermal bulk polymerization at a temperature at which decomposition did not occur. To satisfy this condition, the side of the benzene ring was linked with an ester bond, not an amide bond, and an amide bond was introduced into the diol. When the amide bond was introduced into the diol, DMT could be used as a counterpart of the polymerization. Since the melting point of DMT was 140 °C, the process temperature could be drastically lowered and the possibility of successful thermal bulk polymerization could be greatly increased.
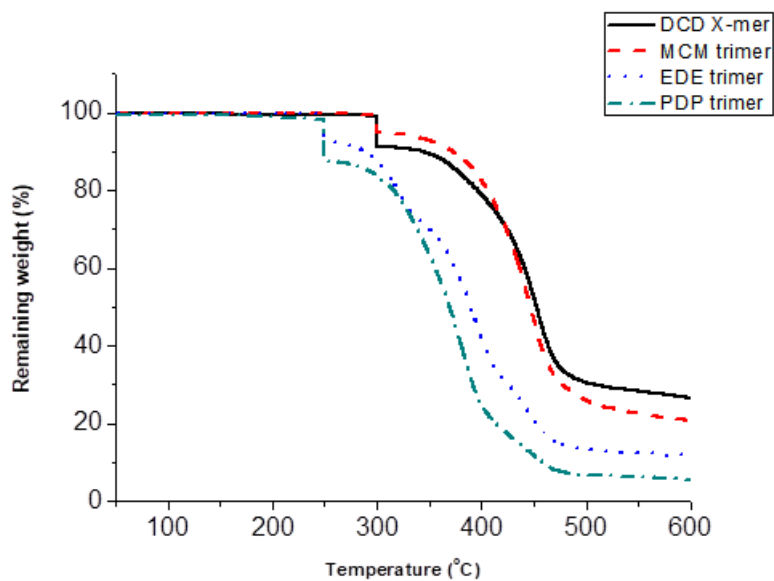
**Figure 3.** TGA thermograms of terephthalamide monomers used for thermal bulk polymerization
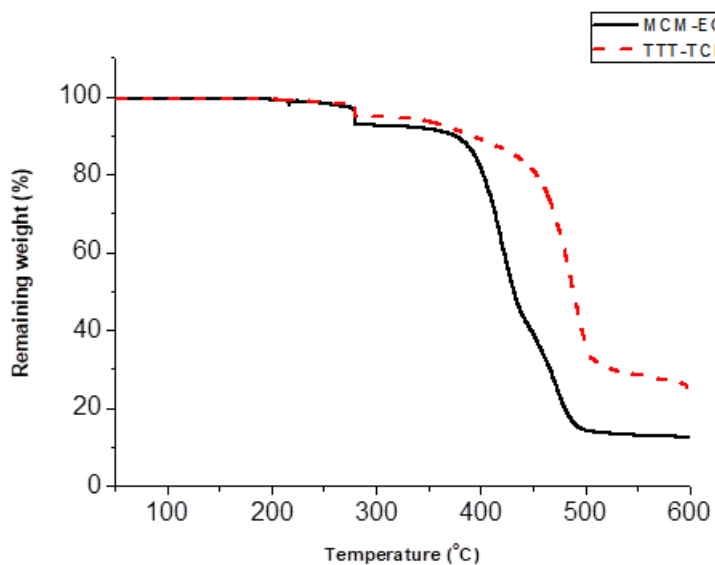
Figure 4. TGA thermograms of solution polymerization products

3.3 Synthesis of Tailor-made Diols Containing Amide Bonds and

   Thermal Properties of Diols

The newly proposed reaction was conducted by the simple aminolysis reaction between amino-alcohol and dimethyl ester as shown in Scheme 1. [28] A total of eight diols were synthesized by varying the carbon chain length of the amino-alcohol and dimethyl esters which were bio-based molecules with the exception of 3-amino-1-propanol and dimethyl suberate, and it was confirmed by NMR analysis that all of the diols were successfully synthesized. Thermal analysis was performed in order to evaluate the difference between the melting point and the decomposition temperature and to confirm the tendency of this difference according to the carbon chain length. The melting point and the decomposition temperature of each diol were listed in Table 3. Based on the same dimethyl ester, diols synthesized with propanolamine showed the lower melting point and higher decomposition temperature than diols synthesized with ethanolamine. For this reason, the longer the length of the carbon chain in the diol was the bigger ΔT value. The correlation between the increase in the length of the carbon chain in the diol and the melting point appeared to be negligible. It was considered that this result was because the effect obtained by increasing the molecular weight and the effect of how well the amide bonds were

structurally packed and exhibited strong hydrogen bonds were in conflict with each other. Four diols, EAE, PAP, ESuE, PSuP diol, were selected to facilitate the set up of process temperature for thermal bulk polymerization based on thermal properties, especially ΔT value.
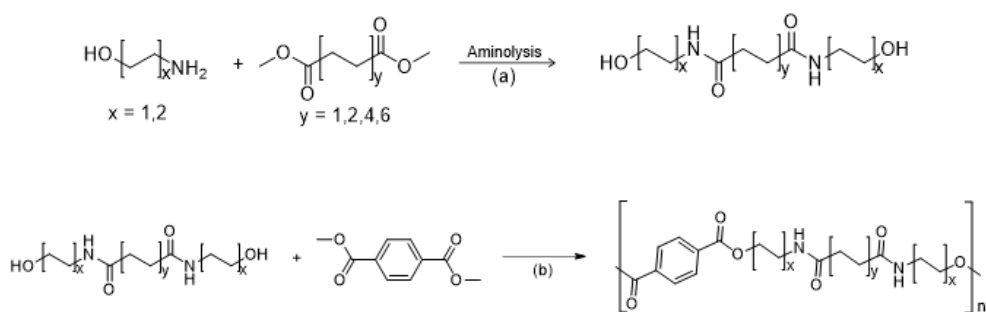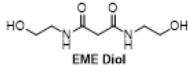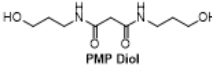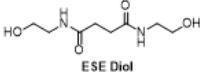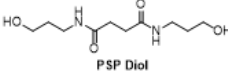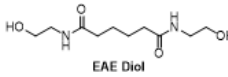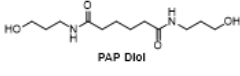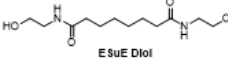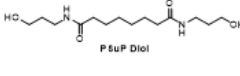

(a) Aminolysis 120 °C, 12 h
(b) Oligomerization 170 °C, 3.5 h / Polymerization 200 ~ 290 °C, 1.5 h, Under Vacuum (< 1 torr)

Scheme 1. Synthetic scheme of diols and polymerization thereof

Table 3. Thermal properties of diols and polymerization products

No	Bio-based diol	T_m (℃)	T_d (℃)	$\triangle T$ ($T_d - T_m$)	Solution Polymerization	Thermal Bulk Polymerization
1	EME Diol	128.88	170.13	41.25	O ($T_{d5\%}$: 220.07 ℃)	X
2	PMP Diol	99.09	164.29	65.2	O ($T_{d5\%}$: 220.11 ℃)	X
3	ESE Diol	157.65	187.41	29.76	O ($T_{d5\%}$: 214.29 ℃)	X
4	PSP Diol	144.32	202.21	57.89	O ($T_{d5\%}$: 238.61 ℃)	X
5	EAE Diol	139.13	218.54	79.41	O ($T_{d5\%}$: 216.15 ℃)	O (T_m : 250 ℃ , $T_{d5\%}$: 291.58 ℃)
6	PAP Diol	134.15	217.38	83.23	O ($T_{d5\%}$: 242.91 ℃)	O (T_m : 260 ℃ , $T_{d5\%}$: 323.19 ℃)
7	ESuE Diol	141.62	219.24	77.62	O ($T_{d5\%}$: 309.11 ℃)	O (T_m : 230 ℃ , $T_{d5\%}$: 340.01 ℃)
8	PSuP Diol	133.10	245.54	112.44	O ($T_{d5\%}$: 282.22 ℃)	O (T_m : 300 ℃, $T_{d5\%}$: 359.95 ℃)

T_d : The temperature at which decomposition begins, T_m of diols : Measured using DSC, T_m of thermal bulk polymerization product : Measured using the melting point analyzer
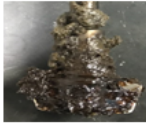
3.4 Polymerization of Poly(ester-amide)s with Tailor-made Diols

As shown in Figure 5 and Table 3, all four diols used in the thermal bulk polymerization were found to have a melting point of about 130 to 140 ℃ and a decomposition temperature of 200 ℃. It was expected that oligomerization reaction could proceed stably without decomposition when the polymerization process was carried out with DMT having a melting point of 140 ℃. In addition, similar to the case of using compounds with a terephthalamide structure, the solution polymerization was performed using eight diols to polymerize the oligo-polymer, and the decomposition temperature was measured. In the case of oligo-polymers in which the solution polymerization was carried out using four diols used in the thermal bulk polymerization, it was assured once again that the thermal polymerization was possible to proceed because the decomposition starting temperature was more than 200 ℃ and the difference from the melting point was more than 60 ℃ as can be seen in Figure 6 and Table 3.

After sufficient analysis, the thermal bulk polymerization was conducted by the same process as PET. As a result, poly(ester-amide)s were successfully polymerized with all four diols without carbonization for the first time since the research. In order to obtain high conversion, the

oligomerization proceeded at a temperature of 170 °C, which was 30 °C higher than the melting point of the reactants, and the polycondensation step was conducted at a temperature of 200 °C. The molar compositions and reaction conditions, thermal properties and photographic images of polymers were listed in Table 4.

Table 4. Various information and photographic images of PEAs

No	Monomer molar ratio		Catalyst	Reaction time	Vacuum condition	T_g	T_c	T_m	Photo image
	HO-R-OH	HOOC-R-COOH							
	Bio-based Diol	DMT							
1	EAE Diol (2.1)	1		3.5 h + 1.0 h	1.2 torr	153.9	-	250	
2	PAP Diol (2.1)	1	Maganese acetate / Antimony triglycolate or Titanium butoxide	3.5 h + 2 h	0.5 torr	147.2	-	260	
3	ESuE Diol (2.1)	1		3.5 h + 1.5 h	0.7 torr	$\triangle^1$	-	230	
4	PSuP Diol (2.1)	1		3.5 h + 1.5 h	0.4 torr	134.1	-	300	

$\triangle^1$: Several peaks observed, T_m of thermal bulk polymerization product : Measured using the melting point analyzer
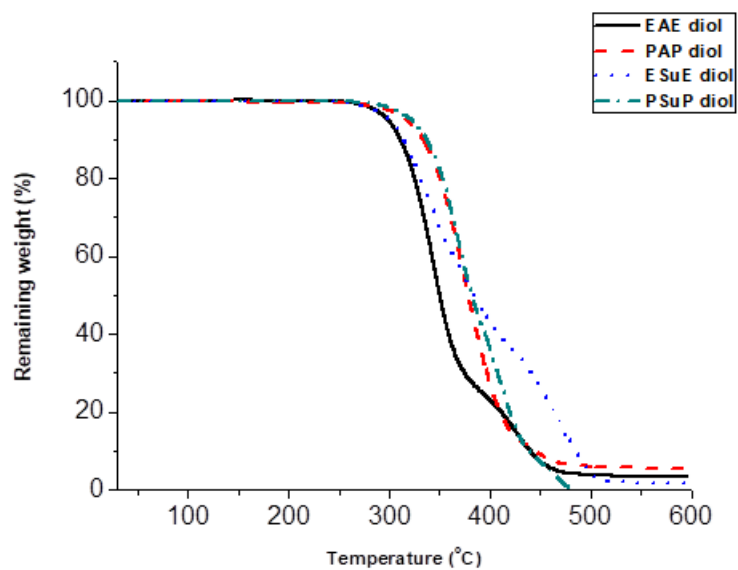
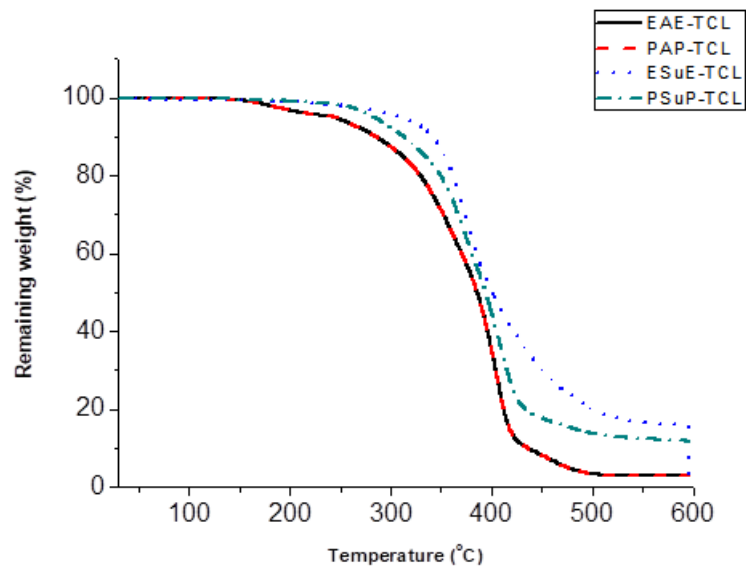**Figure 5.** TGA thermograms of diols used in the thermal bulk polymerization

Figure 6. TGA thermograms of oligo-polymers through solution polymerization

3.5 Establishment Further Research Direction through Representative Compound Selection and Various Analyses Thereof

Tailor-made diols could be prepared by variously controlling the length of carbon chains. Therefore, in order to know how to proceed with changing the carbon chain length of the diol in the future, the representative compound was selected and various analyses thereof was carried out, especially mechanical properties which were a key factor to determine the length of the carbon chain in diol. The selected representative compound was the product of thermal bulk polymerization between PSuP diol and DMT. In order to increase the degree of polymerization of the selected representative compounds, a total of three considerations were taken into account. The first was to reset the process temperature. In the same way as the process temperature of the regular PET, the process temperature of the polycondensation step was fixed at 200 ℃. In this case, the viscosity of the reaction mixture inside the reactor was elevated so that the reaction mixture stuck to the impeller before sufficient reaction could take place, and the reaction was terminated spontaneously. To overcome this phenomenon, it was important to lower the melt viscosity of the reaction mixture by continuously raising the process temperature of the polycondensation step.[29] One thing to note here was that the process temperature should be

raised to the point where the reaction mixture in the reactor was not decomposed as shown in figure 7. The second thing to consider was the speed control of stirring. When the polymerization was performed under a vacuum condition, it was necessary to effectively remove the air bubbles generated in the reaction mixture. For this purpose, the polymerization should proceed at a stirring speed of 60 rpm, which was lower than 200 rpm, which was the stirring speed of the generally used overhead stirrer. In addition, the overhead stirrer could be possible to measure the torque value so that the viscosity of the reaction mixture could be measured, which could effectively lower the melt viscosity by effectively raising the reaction temperature. In order to satisfy these conditions, a Heldoph, Hei-torque value 100 was used as an overhead stirrer when the polymerization of the representative compound was carried out. The final note was the use of catalysts. Polycondensation reaction was carried out by using antimony (Sb) catalyst and titanium (Ti) catalyst, which were two widely used catalysts.[30-33] The comparative evaluation between two different catalysts was conducted with the representative compound and the product of the polymerization between EAE diol and DMT as listed in Table 5. When the Ti-based catalyst was used, it exhibited a relatively severe discoloration and it was difficult to control the process temperature because the activity of the

Ti catalyst was higher than that of the Sb catalyst.[33],[34] For this reason, antimony triglycolate was selected as the catalyst to use for the polymerization of the model compound, and various analyses were carried out using the product of the polymerization with reference to the above three considerations.
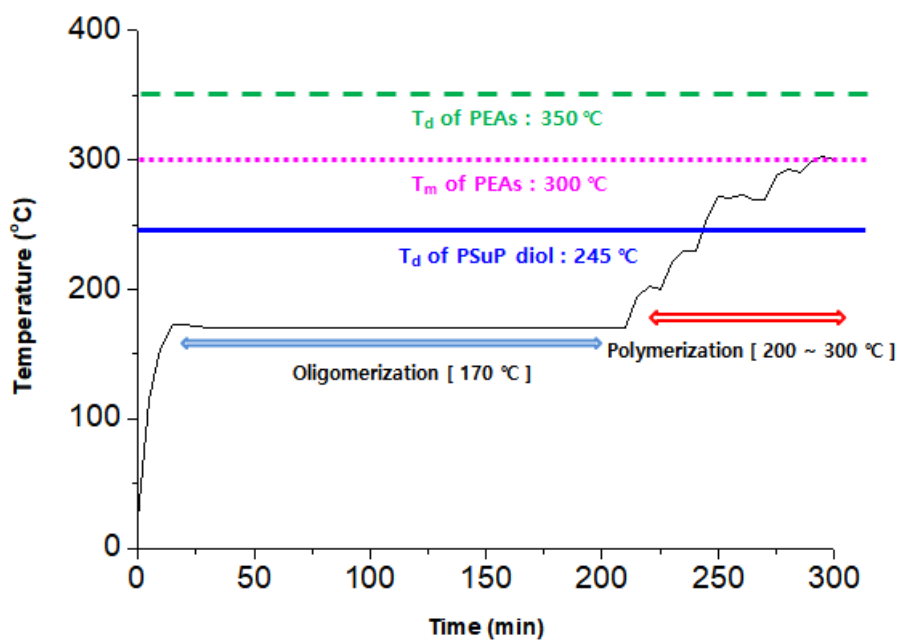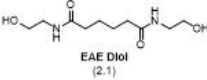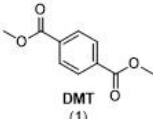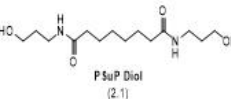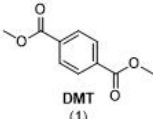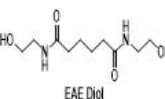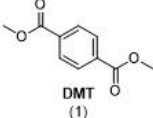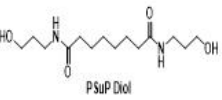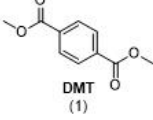

Figure 7. Temperature profile of the polymerization (Representative compound)

Table 5. The comparative evaluation between Ti catalyst and Sb catalyst

Catalyst	Monomer (Diol)	Monomer (Diacid)	Color	Reaction profile	Thermal Property
Titanium butoxide	EAE Diol (2.1)	DMT (1)		200 ~ 240 ℃ Below 1 h 1.2 torr	T_g : 134.89 ℃ $T_{d5\%}$: 291.58 ℃ T_m : 250 ℃
	P SuP Diol (2.1)	DMT (1)		200 ~ 240 ℃ 1.5 h 0.37 torr	T_g : 134.07 ℃ $T_{d5\%}$: 350.50 ℃ T_m : 300 ℃
Antimony triglycolate	EAE Diol	DMT (1)		200 ~ 270 ℃ 1.25 h 0.47 torr	T_g : 153.97 ℃ $T_{d5\%}$: 302.94 ℃ T_m : 250 ℃
	P SuP Diol	DMT (1)		200 ~ 270 ℃ Below 2 h 0.39 torr	T_g : 135.14 ℃ $T_{d5\%}$: 353.38 ℃ T_m : 300 ℃

T_m of thermal bulk polymerization product : Measured using the melting point analyzer

First of all, GPC analysis was carried out to measure the molecular weight of the model polymer. After completely dissolving the representative polymer in formic acid with 1:100 v/v concentration, the solution precipitated in an excess of 1:1 mixture of distilled water and methanol and filtered out. The filtered solid was used for sample preparation and after that, the sample for GPC analysis was prepared according to the method described in experiments. Since GPC instrument capable of analyzing HFIP diluted chloroform did not exist in the laboratory undergoing the experiments, the GPC analysis was conducted at Hyosung Inc. As a result, it was confirmed that the model polymer having a value of M_n: 42,400, M_w: 54,600, and PDI: 1.28, was synthesized as can be seen in Figure 8 and Table 6. Secondly, The FT-IR analysis of the model polymer was conducted. It was confirmed that the representative polymer was successfully polymerized by observing the carbonyl peak of the ester bond detected at 1710 cm^{-1} and the carbonyl peak of the amide bond detected at 1635 cm^{-1} as shown in Figure 9. Third, three different thermal analyses were performed. Both DSC and TGA were programmed at both healing and cooling rates of 10 °C/min. In the DSC trace of Figure 10-(a), only the glass transition temperature was observed, and no crystallization and melting peak were observed. It was not expected that the representative polymer would be the

amorphous polymer based on the structure of the polymer. Therefore, DSC was carried out after sufficient annealing for 24 h at the temperature of the glass transition temperature to crystallize the polymer.[35],[36] Here again, the crystallization and melting peak were not observed. By this reason, the representative polymer was considered to be an amorphous polymer. The glass transition temperature, 134.07 °C, was relatively higher than that of regular PET at a level of 70 °C, and thus it was considered that PEAs could be used at a higher temperature than PET. The thermal stability of the representative compound was determined by TGA as can be seen in Figure 10-(b). The degradation temperature at 5 wt % loss of original weight was 350.50 °C. In comparison with the melting point of diols and DMT, it was feasible to process polycondensation in the range of 200 °C–300 °C without consideration of thermal degradation. Since no melting point was observed in the DSC trace the melting point was indirectly confirmed by using the melting point analyzer. Because the above equipment used a capillary tube which was not easy to see by photo image, it was more easily seen that the representative polymer was placed between the cover glass and placed on the hot plate. As shown in Figure 10-(c), the representative polymer became sticky above about 130 °C and started to melt partially from about 280 °C and completely melted at around 300 °C.

Table 6. The molecular weight and PDI value of the representative polymer

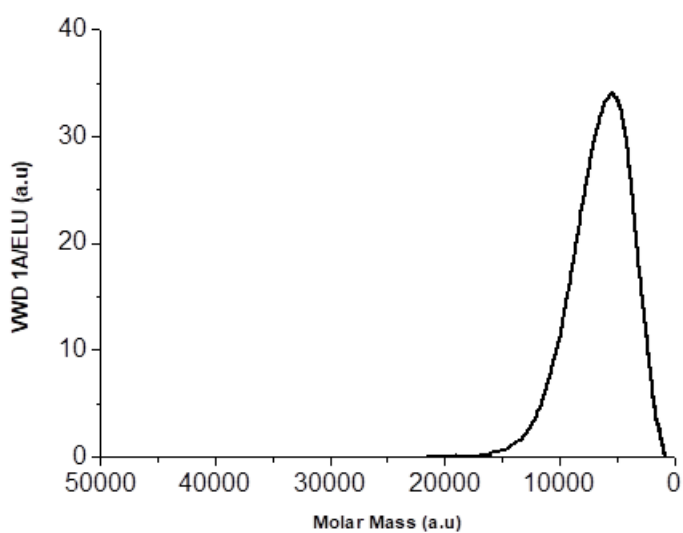| Sample	M_n	M_w	M_z	PDI
Model Polymer	42,400	54,600	66,100	1.28

Figure 8. Elution curve for the representative polymer (HFIP/chloroform = 2/98 (v/v))
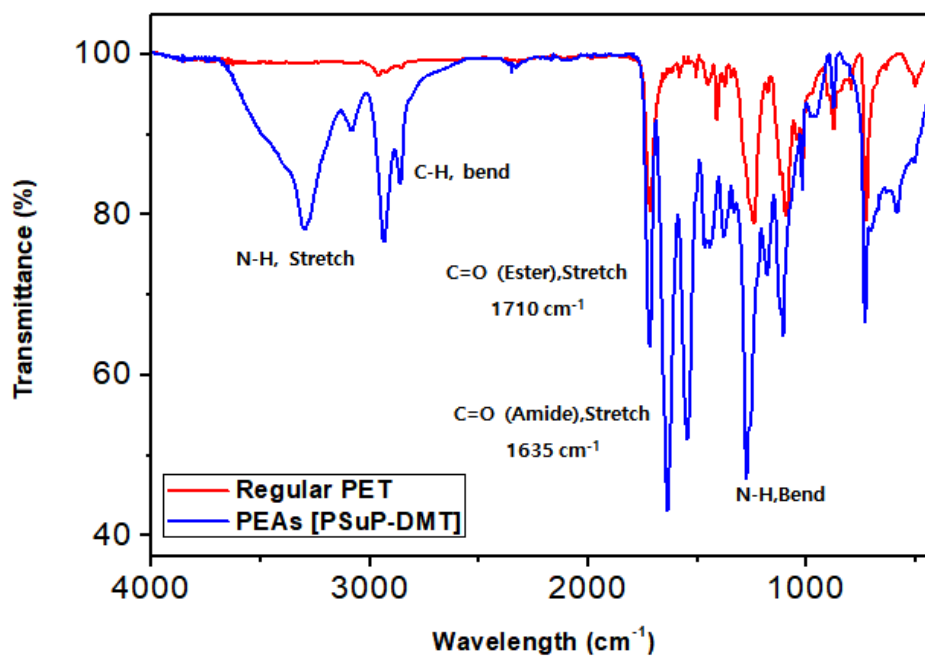
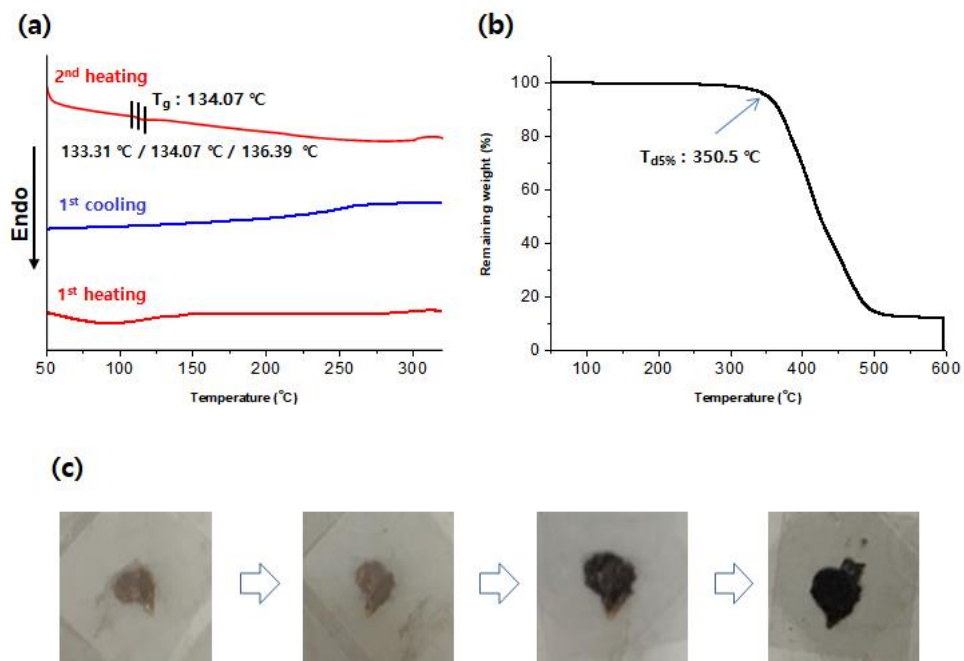**Figure 9.** FT-IR spectra of the representative polymer and regular PET

Figure 10. Thermal analysis of the model polymer; (a) DSC traces, (b) TGA thermogram, (c) Photo image of the representative polymer on the hot plate at 25 ℃, 130 ℃, 280 ℃, 320 ℃ from left to right

The most important analysis for establishing the next research direction was the evaluation of mechanical properties of the representative polymer. The representative polymer was polymerized on a large scale, the sum of total reactants was approximately 100 g scale, in order to prepare specimens for the evaluation of mechanical properties. The special glassware capable of nitrogen ejection was used for entire sampling the polymer, and the limit of the viscosity of the polymer capable of ejecting nitrogen was determined, and the representative polymer was sampled through nitrogen ejection at that viscosity. The regular PET used as the control group was polymerized under the same conditions and sampled by proceeding the nitrogen ejection at the same viscosity value as the model polymer. The tensile test specimens were prepared by using an injection molding machine capable of making tensile test specimens using about 40 g-50 g of polymer samples. In the case of regular PET, the temperature setting of the injection molding process was previously completed and the specimens were successfully manufactured. However, in the case of the representative polymer, since it was the first attempt, the process temperature of injection molding was failed to set up, therefore, the production of specimens also failed. The evaluation of mechanical properties will be conducted as soon as the preparation of specimens was completed. If the satisfactory mechanical properties superior

to regular PET are observed, it is possible to increase the carbon chain length of the tailor-made diol and to use various candidate compounds. When the mechanical properties are relatively low, the mechanical properties of polymer which is polymerized with EAE diol will be evaluated.

4. CONCLUSION

The aim of the research was to make poly(ester-amide)s, which had both advantages of polyester and polyamide, by the thermal bulk polymerization which had a high industrial competitiveness with using bio-based feedstocks. For the better mechanical properties than PET, synthesis of monomers which had terephthalamide structure proceeded in the initial stage of the research. However, the monomers of terephthalamide structure had quite a high melting point compared with the decomposition temperature, resulting in the decomposition of the amide bond at the temperature of thermal bulk polymerization and carbonization without progressing the polymerization because if the dense-packing between the aromatic rings and the strong hydrogen bonding due to amide bonds. In addition, the counterpart of the polymerization was fixed with EG, which was known to degrade at the polymerization temperature. In order to overcome these problems, the amide bond was introduced into the aliphatic diol to lower the melting point of monomer, and DMT was used as the counterpart of the polymerization to drastically lower the process temperature. Furthermore, the decomposition temperature of all of monomers and oligo-polymer polymerized by all the monomers were measured in advance, and the thermal bulk polymerization

was performed with using four kinds of tailor-made diols that were sufficiently different in melting point and decomposition temperature by setting the process temperature at which no decomposition occurred during the polymerization. As a result, the thermal polymerization of PEAs with all four diols succeeded in the same process as regular PET. It was confirmed that successful polymerization could be performed even if another diol was used if the value of ΔT showed a sufficient difference. Various analyses were conducted by selecting the polymerization product of PSuP diol and DMT among synthesized PEAs as the representative polymer. The FT-IR analysis confirmed that both the ester bond and the amide bond were retained and the GPC analysis confirmed that the M_w value of the model polymer was approximately 55,000 (PDI: 1.28). The thermal analysis showed that the glass transition temperature was nearly twice as high as that of PET, which was expected to be useful with a much higher practical temperature range and the representative compound was analyzed as an amorphous polymer. Currently, specimens for the tensile test are being manufactured for evaluation of mechanical properties, and as soon as the production of specimens is completed, the mechanical properties will be evaluated and additional experimental directions are being planned.

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국문 요약

재생 가능한 자원을 기반으로 한 화학 물질 및 고분자 재료에 대한 관심이 높아지면서 바이오 기반 물질들에 대한 많은 연구들이 진행되고 있다. 전 세계 난분해성 바이오 플라스틱 생산량 1,2 위는 폴리에틸렌테레프탈레이트와 폴리아마이드이다. 폴리에틸렌테레프탈레이트는 낮은 물성과 유리전이온도를 가지는 명확한 단점을 보유하고 있다. 이러한 단점을 보완하기 위한 방법 중 하나로 폴리에스터와 폴리아마이드를 결합한 폴리에스터아마이드를 중합하고자 하는 연구들이 진행되고 있다. 현재까지, 지방족 단량체를 이용한 폴리에스터아마이드 중합에 관한 연구 외에 방향족 단량체를 포함시킨 중합에 관한 연구는 거의 진행되고 있지 않다. 폴리에틸렌테레프탈레이트 보다 우수한 물성의 바이오 플라스틱 개발을 위해 본 연구에서는 비식용 바이오 기반 물질인 아미노산과 다이메틸에스터를 기반으로, 폴리에스터아마이드 중합을 위한 단량체를 선정 및 합성하고 이의 합성을 진행하였다. 연구 진행 초기에는, 보다 우수한 물성을 보유하고자 테레프탈아마이드 형태의 단량체를 합성하여 중합을 시도하였다. 테레프탈아마이드 형태의 단량체는 벤젠 고리 사이의 우수한 적층성과 반복되는 아마이드 결합으로 인한 수소 결합으로 인해 높은 융점을 보유하여 용융 공정으로 중합을 진행 시 분해되는 현상이 발생하기 때문에 열

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중합을 위한 단량체로 부적합하다고 판단하였다. 이를 개선하고자 아마이드 결합을 지방족 다이올에 도입시켜 융점을 낮추고, 중합 대응물로 융점이 낮은 다이메틸테레프탈레이트를 선정하여 열 중합을 위한 용융 공정 온도를 대폭 낮추었다. 중합에 사용되는 모든 단량체와 용액 중합을 통해 합성한 올리고폴리머의 열적 안정성을 평가하여 녹는점과 분해 온도가 충분한 차이를 나타내는 4 종류의 다이올을 선정하였고, 이를 이용한 열 중합을 진행하였다. 폴리에틸렌테레프탈레이트와 동일한 공정으로, 4 종류의 다이올 모두 열 중합을 성공적으로 진행 완료하였고 대표 중합체를 선정하여 여러 분석을 진행하였다. 적외선 분광법을 통해, 해당 고분자가 에스터 결합과 아마이드 결합 둘 모두를 보유함을 확인하였고, 젤 투과 크로마토그래피 분석을 통해 중량평균분자량이 약 55,000, 다분산지수는 1.28의 값을 가지는 고분자가 중합되었음을 확인하였다. 열 분석을 통해 유리전이온도가 폴리에틸렌테레프탈레이트에 비해 2 배 가까이 높음을 확인하여 훨씬 더 넓은 사용 온도 범위가 요구되는 분야에서의 활용 가능성을 확보하였다.

주요 어: 바이오 플라스틱, 폴리에스터아마이드, 엔지니어링 플라스틱, 바이오기반 고분자 중합, 축합 열 중합

감사의 글

2년 동안의 석사과정 기간 동안 정말 많은 분들의 도움을 받아 연구를 잘 진행할 수 있었습니다. 가장 먼저 부족한 저를 석사과정 기간 동안 이끌어주시고, 가르쳐주신 지도 교수님이신 안철희 교수님께 진심으로 감사 드립니다. 학문, 연구와 관련된 부분 외에도, 연구자가 가져야 할 자세와 마음가짐 그리고 좋은 사람으로 성장하기 위한 인성적인 부분 역시 교수님께 많이 배울 수 있었기에 2년의 석사과정 기간 동안 제가 한층 더 성장할 수 있었습니다. 이어서 진행하게 될 박사과정에서도 교수님께 많은 가르침을 받아 좋은 연구자가 될 수 있도록 하겠습니다. 또한 바쁘신 와중에도 저의 공학석사 학위 논문 심사에 참석해주시고 많은 조언을 해주신 장지영 교수님과 김재필 교수님께도 진심으로 감사 드립니다.

NBML에서 대학원 생활을 보내며 정말 좋은 사람들을 만나 많은 도움과 추억을 받은 것 같습니다. 먼저 저에게 처음으로 축합중합에 대해 가르쳐주시고, 실험 외에도 많은 것을 알려주신 선호형 그리고 관련 분야의 전문가로서 항상 아낌없이 조언을 해주시는 김무송 팀장님, 두 분에게 연구 관련하여 많은 도움을 받아 연

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구를 잘 진행할 수 있었습니다. 또한 다양한 분야에 대해 잘 아시고 항상 필요한 조언을 주시는 인재형과 NBML 방장으로서, 솔선수범하여 열심히 연구하시는 성익이형 그리고 실험실의 든든한 맏형으로 늘 저를 챙겨주시는 성훈이형, KIST 에 있어 자주 못 보지만 볼 때마다 반가운 한희형, 같이 입학하여 의지가 되는 동기 소연이와 마지막으로 열심히 하는 막내 창현이까지 많은 분들의 도움을 받아 석사과정을 잘 마무리 할 수 있었습니다. 앞으로 진행할 박사과정에도 같이 잘 연구하여 좋은 결과를 도출하고, 건강하고 즐겁게 실험실 생활을 이어나갔으면 좋겠습니다.

마지막으로 뒤에서 묵묵히 항상 내편이 되어주고, 오랜 시간 동안 저를 믿고 지지해준 저의 가족과 제가 사랑하는 사람들에게 진심으로 감사하고 사랑한다는 말 전하고 싶습니다. 앞으로도 더 좋은 사람이 될 수 있도록 노력하겠습니다.

감사합니다.

2019년 1월

김형준 올림