Synthesis and characterization of novel copolyesters, polyalkylene terephthalates using biobased diols

바이오 기반 디올을 활용한 새로운 폴리알킬렌 테레프탈레이트계 코폴리에스터의 합성 및 특성에 관한 연구

2018 년 2 월

서울대학교 대학원
재료공학부
김 지 현
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지도 교수 안 철 희

이 논문을 공학박사 학위논문으로 제출함

2017 년 12 월

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Abstract

Synthesis and characterization of novel copolyesters, polyalkylene terephthalates using biobased diols

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The Graduate School
Seoul National University

Among the various diols from biomass, 1,2-propanediol (1,2-PD), 2,3-butanediol (2,3-BD), and 1,3-butanediol (1,3-BD) were selected as comonomer of copolyester with 1,4-cyclohexane dimethanol (CHDM) and dimethyl terephthalate (DMT) instead of ethylene glycol (EG). As the results, new potentially biobased copolyesters, poly(1,2-propylene 1,4-cyclohexylenedimethylene terephthalate) (P12PCT), poly(2,3-butylene 1,4-cyclohexylenedimethylene terephthalate) (P23PCT), poly(1,3-propanediol 1,4-cyclohexylenedimethylene terephthalate) (P13PCT), and poly(1,4-cyclohexane dimethylene terephthalate) (PCHDMT) were synthesized and characterized.
cyclohexylenedimethylene terephthalate) (P23BCT), and poly(1,3-butylene
1,4-cyclohexylenedimethylene terephthalate) (P13BCT), were synthesized
instead of poly(ethylene glycol-co-1,4-cyclohexanediol methanol terephthalate)
(PECT also called PETG). Furthermore, using isosorbide (ISB) with 1,2-PD,
novel copolyesters with more biobased contents and higher $T_g$, poly(1,2-
propylene isosorbide 1,4-cyclohexylenedimethylene terephthalate)
(P12PICT), and poly(1,2-propylene isosorbide terephthalate) (P12PIT),
were synthesized.

The compositions of each copolyester were confirmed using $^1$H-NMR
spectroscopy, and the detailed structure was analyzed using 2D NMR
spectroscopy. If possible, $^{13}$C-NMR spectroscopy analysis was performed
for the microstructure and randomness in the sequences of the copolymers.
The thermal properties, mechanical properties, and crystallinity of the
copolyesters were analyzed using differential scanning calorimetry,
thermogravimetric analysis, and universal testing machine.

In case of P12PCT and P23BCT compared to PECT, depending on the
number of the lateral methyl groups and the contents of the ethylene diol
units, the copolyesters displayed different densities, glass transition
temperatures ($T_g$), degrees of randomness and mechanical properties;
however, a notable difference was not observed in thermal stability or crystallinity.

The catalyst played a key role in the synthesis of P13BCT, the results of polymerization of two catalysts were significantly different depending on side reaction. The mechanism of side reaction was clarified by analyzing the side-product using GC-MS. Depending on the contents of the 1,3-BD units, the copolyesters displayed different densities, glass transition temperatures ($T_g$), crystallinities, and yield strengths; however, no significant difference was observed in thermal stability and Young’s modulus.

Lastly, by introducing ISB into the P12PCT copolyesters, new P12PICT terpolyesters with high $T_g$ were synthesized, and P12PIT copolyesters excluding CHDM were also successfully obtained, they had higher biobased content and displayed higher $T_g$ up to 150℃. Compare to PEICT, P12PICT had higher ISB contents and $T_g$ at same ISB feed ratio, even if compared to PEICT with same ISB content, P12PIT displayed higher $T_g$ due to the lateral methyl group. In case of P12PIT, the residual ratio of ISB became higher, the copolyester with more ISB and higher $T_g$ could be obtained. These novel copolyesters have adequate molecular weights and nearly random sequence. The rigidity of ISB monomer made
the copolyester stiffer and brittle and produced higher yield strength and Young’s modulus.

**Keywords:** renewable resources, biobased, copolyester, 2,3-butanediol, 1,2-propanediol, isosorbide, 1,3-butanediol, 1,4-cyclohexanediolmethaneol

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<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>1,2-PD</td>
<td>1,2-Propanediol</td>
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<td>1,3-PD</td>
<td>1,3-Propanediol</td>
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<td>1,4-BD</td>
<td>1,4-Butanediol</td>
</tr>
<tr>
<td>2,3-BD</td>
<td>2,3-Butanediol</td>
</tr>
<tr>
<td>CHDM</td>
<td>1,4-Cyclohexanediethanol</td>
</tr>
<tr>
<td>COSY</td>
<td>Correlation spectroscopy</td>
</tr>
<tr>
<td>DBTO</td>
<td>Dibutyltin oxide</td>
</tr>
<tr>
<td>DMT</td>
<td>Dimethyl terephthalate</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>EG</td>
<td>Ethylene glycol</td>
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<td>FDCA</td>
<td>2,5-Furandicarboxylic acid</td>
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<td>GC-MS</td>
<td>Gas chromatography-mass spectrometry</td>
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<tr>
<td>HMF</td>
<td>Hydroxymethylfurfural</td>
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<td>HSQC</td>
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<td>ISB</td>
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<tr>
<td>TPA</td>
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<td>WAXD</td>
<td>Wide angle X-ray diffraction</td>
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Chapter 1.

Introduction
1.1. Background of research of biobased materials and renewable building blocks

The last two decades have seen growing trend towards renewable resources and biorefinery because the concern about lack of fossil fuels and global warming (greenhouse effect, cause further warming and induce many changes in the global climate system)\(^{[1]}\) promoted research on alternatives to petrochemicals.\(^{[2-12]}\) As shown in Fig. 1-1, there are various routes for production (namely, gasification, pyrolysis, and hydrolysis) of chemicals from biomass compared to fossil resources.\(^{[7, 8]}\) The platform concept is similar to each other, and the technology advance in the diverse area of genetics, biotechnology, process chemistry, and engineering led to new manufacturing concept for converting renewable biomass to valuable fuels and products, generally referred to as the biorefinery (Fig. 1-2)\(^{[3]}\). The concept of biorefinery was defined as “the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, and materials) and bioenergy (biofuels, power and/or heat)” by IEA Bioenergy Task 42,\(^{[10]}\) which is an international collaboration with 11 countries aimed to promote sustainable biorefinery systems market implementation. Advanced biorefineries have enabled systematic research and development.
Fig. 1-1. Routes for the production of chemicals from fossil feedstocks and biomass [8].
Fig. 1-2. Concept of the biorefinery. (J. Ragauskas et al. Science 2006 [3])
of a wide range of bio-based building blocks, which are key platform chemicals for the novel biobased industry.\textsuperscript{[2, 5, 6, 10]}

Of the various renewable resources, carbohydrates are particularly convenient raw materials because they are readily available, relatively inexpensive, and present functional diversity as an abundant natural product. The US Department of Energy (DOE) published in 2004 the “Top 10” value-added chemicals from sugar, which are a final group of 15 from 30 viable candidates among the initial list of over 300 possible products.\textsuperscript{[2]} In 2010, an updated report released the “Top 10+4” list which removed certain chemicals with minor growth market and added newly selected chemicals with high potential in industries such as ethanol and lactic acid (Table 1-1).\textsuperscript{[6]} Developing a list of specific target chemicals embraced product identification as a guide for research and also reflected a methodology that included factors such as known processes, economics, industrial viability, size of markets, and the ability of a compound to serve as a platform for the production of derivatives.

For example, furans hydroxymethylfurfural (HMF) is one of promising biorefinery platform chemicals, and its interest and researches were rapidly increased since the 2000s.\textsuperscript{[13, 14]} As shown Scheme 1-1\textsuperscript{[13]}, HMF could be an intermediate of various essential furan chemicals
Table 1-1. The DOE “Top 10+4” key chemicals from carbohydrates through new criteria\[6\]

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</table>

\[a\] +++ = Good performance against criterion; ++ = emerging performance against criterion; + = lower performance against criterion.
Scheme 1-1. Hydroxymethylfurfural (HMF) as a platform chemical.\textsuperscript{[13]}
including 2,5-furandicarboxylic acid (FDCA), 5-hydroxymethylfuroic acid (HMF), and 2,5-bishydroxymethylfuran (5), and also produced some critical nonfuranic compounds such as levulinic acid (8) and adipic acid (9). Among them, FDCA with HMF especially considered as "sleeping giant" because of their enormous potential for the production of green plastics. Especially, FDCA is one of the most desirable biobased monomers as a substitute for terephthalic acid (TPA).\textsuperscript{[15, 16]} TPA, as it is well known, is a raw material of commodity polyesters, \textit{i.e.}, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT).

Scheme 1-2 displays sorbitol and its derivatives as another example of platform chemicals\textsuperscript{[17, 18]}. Among them, isosorbide (ISB) is the most attractive chemical because of its high stability and two functional hydroxyl groups that can be modified into other functional groups, which lead to a vast variety of monomers for novel polymers.\textsuperscript{[19]} ISB could be obtained by twofold dehydration of sorbitol via sorbitan and widely used as a monomer of polyester due to the rigidity, and high stability stemmed from two \textit{cis}-connected tetrahydrofuran rings.
Scheme 1-2. Sorbitol and isosorbide as a platform chemical.\cite{17, 18}
1.2. Renewable plastics and bio-based copolyesters

There are many types of research and reviews on various biobased plastic\cite{12,20-23}, among them, polyesters are definitely the most attractive and promising polymer because the monomers are readily accessible compared to other polymers such as polyolefin or polyamide.\cite{24} Also, the development of biobased polyesters has been accelerated by their unique and vast properties such as biodegradability and diverse application like packaging and fiber. Poly(lactic acid) (PLA)\cite{25} and poly(hydroxyalkanoates) (PHAs)\cite{26,27} are representatives; they are the primary drivers of the growth in the field of biobased, biodegradable plastics.\cite{28}

Many biobased polyesters were already commercialized as shown Fig. 1-3, which presents the global production capacities of bioplastics in 2017.\cite{29} Including PLA and PHAs, most of the bioplastics in Fig. 1-3 are polyesters, i.e., PET, poly(butylene succinate) (PBS), and poly(butyrate adipate terephthalate) (PBAT). In 2009, the Coca-Cola introduced ‘Plant Bottle’\cite{30}, which was made partially biobased PET using ethylene glycol (EG) converted from sugarcane. Moreover, by replacing TPA with FDCA, they have been tried to develop 100% biobased PET, actually poly(ethylene furanoate) (PEF), which shows superior gas barrier properties.\cite{31-33}
Fig. 1-3. Global production capacities of bioplastics 2017 (by material type).[29]

*Bio-based PP and PEF are currently in development and predicted to be available in commercial scale in 2020.
Beside polyesters in Fig. 1-3, poly(trimethylene terephthalate) (PTT)$^{[34]}$ and PBT were also commercialized as partially biobased polyesters using 1,3-propanediol (1,3-PD)$^{[35]}$ and 1,4-butanediol (1,4-BD)$^{[36]}$ from renewable resources. Especially, PTT has been attracting in fiber application due to unique properties, such as better elastic recovery and lower modulus versus PET and PBT stemmed from the difference of molecular structure. Although these poly(alkylene terephthalate)s are not 100% biobased, they are easily switchable (drop-in) from petroleum-derived ones and keep excellent properties as engineering thermoplastic material due to the rigid aromatic structure.

Moreover, ISB is also attractive monomer of polyester as previously mentioned. The polyesters using ISB would be reviewed in detail later. (Chapter 4.1)
1.3. Research Objectives

An objective of this study was to investigate new biobased copolyesters; five new copolyesters were synthesized by using 1,2-propanediol (1,2-PD), 2,3-butanediol (2,3-BD), and 1,3-butanediol (1,3-BD) in place of EG as a new monomer. With 1,3-PD and 1,4-BD, 1,2-PD are also natural metabolites that are directly produced from different bio-resources[37]; there are many results regarding the fermentation method for the production of them using various species of microorganisms from diverse biomass sources.[38-41] However, few studies have explored to apply polymerization of polyester, and most of these studies have suffered from the poor reactivity stemmed secondary diol.

To overcome this obstacle, 1,4-cyclohexanediol (CHDM) containing primary hydroxyl groups had been incorporated as a comonomer. CHDM is one of the essential commercial diols that is common in a variety of valuable commercial polyesters including poly(ethylene 1,4-cyclohexylenedimethanol terephthalate) (PECT, usually called PETG).[42, 43] CHDM typically comprises 70 % trans and 30% cis isomers, and its cyclohexane ring flips increase the chain mobility, resulting in better stress relaxation and mechanical properties. Recently, Yoon et al.[44, 45]
copolymerized CHDM with TPA, EG, and ISB to synthesize high $T_g$ biobased copolyester, poly (ethylene isosorbide 1,4-cyclohexylene dimethylene terephthalate) (PEICT), which was already commercialized by SK Chemicals. CHDM was used to overcome the low reactivity of ISB. CHDM was also copolymerized with FDCA and EG to improve the properties of PEF.\cite{46, 47}

Chapter 2 describes the synthesis and characterization of two potentially biobased copolyesters poly(1,2-propylene 1,4-cyclohexylene dimethylene terephthalate) (P12PCT) and poly(2,3-butylene 1,4-cyclohexylenedimethylene terephthalate) (P23BCT), having the same ethylene skeletal structure as PETG, were synthesized based on 1,2-PD or 2,3-BD with CHDM. Depending on the number of the lateral methyl groups and the contents of the ethylene diol units, the copolyesters displayed different density, glass transition temperature ($T_g$), degrees of randomness and mechanical property. The most notable effect resulting from the lateral methyl group was the outstanding increase in $T_g$.

In chapter 3, using 1,3-BD instead of 2,3-BD new copolyester series, poly(1,3-butylene 1,4-cyclohexylenedimethylene terephthalate) (P13BCT) was synthesized, and their polymerization results were notably different depending on the type of catalyst. The GC-MS analysis of by-product was
investigated to identify the cause of the difference.

In chapter 4, isosorbide was introduced to synthesize novel copolyesters with high $T_g$. First, polymerization of 1,2-PD with CHDM, ISB, and dimethyl terephthalate (DMT) yielded terpolyester series, poly(1,2-propylene isosorbide 1,4-cyclohexylenedimethylene terephthalate) (P12PICT) compared to PEICT. Then except CHDM, poly(1,2-propylene isosorbide terephthalate) (P12PIT) was polymerized with higher $T_g$ than other copolyesters.
Chapter 2.

Novel biobased copolyesters based on 1,2-propanediol or 2,3-butanediol with the same ethylene skeletal structure as PETG
2.1. Introduction

After the oil crisis in the 1970’s, researches on biomass and renewable resources steadily increased. Recently, the awareness that the still growing use of fossil fuels and emission of greenhouse gases is affecting global climate change is driving the search for sustainable, renewable feedstocks.[4, 21, 48] Among various resources for biomass, carbohydrates are considered as a first-generation feedstock, and much research has focused on using similar key chemicals such as HMF, lactic acid, and sorbitol.[2, 6, 12, 49]

Diols are an essential and valuable feedstock because of their broad applications as biofuels, chemicals, and monomers of polymers, including polyester.[24, 37] Among the various alkylene diols, 1,2-PD and 2,3-BD are natural metabolites that are directly produced from different bio-resources and have the same skeletal structure as EG, the widely used chemical component of PET. There are many results regarding the fermentation method for the production of 1,2-PD and 2,3-BD using various species of microorganisms from diverse biomass sources such as xylose, glucose, and glycerol.[37-40]

A limited number of researches on polyesters using 1,2-PD or 2,3-BD as monomer has been reported. For example, 1,3-PD is a well-known
biobased monomer for PTT; however, there are insufficient results employing 1,2-PD as a monomeric unit. Wu et al. investigated the copolymerization based on PBT\textsuperscript{[50]} or PTT\textsuperscript{[51]} with 1,2-PD. In both cases, increasing 1,2-PD units in the copolymers lowered the melting temperature and increased the glass transition temperature. Bin et al.\textsuperscript{[52]} also reported modified PET using 1,2-PD, but the employed amount of 1,2-PD was very low, and no significant copolymerization effect was observed because they considered 1,2-PD as impurities in bio-EG.

The use of 2,3-BD in polymerization with aliphatic acids, such as succinic, adipic and sebacic acid\textsuperscript{[53-55]} or FDCA have been reported\textsuperscript{[16, 56, 57]}. Gibbels et al.\textsuperscript{[56]} performed the melt polymerization of FDCA and 2,3-BD with various catalysts, and the number-average molecular weight (M\textsubscript{n}) increased from 2,000 to 13,000 g mol\textsuperscript{-1} when tin (IV) ethylhexanoate was used with extended reaction time. Recently, Hu et al.\textsuperscript{[54]} synthesized a high molecular weight biodegradable polyester (M\textsubscript{n} = 15,000 - 33,000 g mol\textsuperscript{-1}) using 2,3-BD copolymerized with several aliphatic biobased monomers including a succinic acid; however, most of the other copolyesters had relatively low molecular weights (M\textsubscript{n} < 5,000 g mol\textsuperscript{-1}), probably due to the poor reactivity of the secondary hydroxyl groups in 2,3-BD.

To overcome these obstacles, comonomers containing primary
hydroxyl groups such as CHDM can be incorporated. CHDM typically comprises 70% trans and 30% cis isomers. It is reported that the cyclohexane ring exists in either the chair or boat conformation and flips from an e,e-trans form to an a,a-trans form via a twisted-boat structure at room temperature. These ring flips increase the chain mobility, resulting in better stress relaxation and mechanical properties. Yoon et al. [44, 45] copolymerized CHDM with TPA, EG, and ISB. CHDM was used to overcome the low reactivity of ISB, a typical biobased monomer that is also a secondary diol similar to 2,3-BD. Recently, CHDM was also copolymerized with FDCA and EG to improve the properties of PEF. [46]

In this study, polymerization of 1,2-PD or 2,3-BD with CHDM and DMT yielded two new polyester series, P12PCT and P23BCT, which have the same skeletal structure as PECT (also known as PETG). To explain the influence of lateral methyl groups of ethylene units on polymer properties, the effect of diol composition on the microstructure, thermal properties, crystallinities, and mechanical behaviors of the obtained copolyesters were investigated.
2.2. Experimental

2.2.1. Materials

DMT (99.9%), EG (99.8%), CHDM (99.8%) with 70 mol % of the trans isomer, germanium oxide (GeO$_2$), and dibutyltin oxide (DBTO) were used as received from SK Chemicals (Korea). 1,2-PD (99.5%) and 2,3-BD (99.8%, mixture of stereoisomers) chloroform-$d$ (CDCl$_3$, 99.8%), and trifluoro-acetic acid-$d$ (TFA-$d$) (99.5%) were purchased from Aldrich and used as received.

2.2.2. Synthesis of the copolyesters

The three types of copolyesters, PECT, P12PCT, and P23BCT, were synthesized by melt polymerization in two steps, transesterification and polycondensation. These copolyesters are called PE$_x$CT, P12P$_x$CT, and P23B$_x$CT with the subscripts $x$ standing for their molar contents in ethylene diol units. The corresponding monomers and catalysts were charged into a 1 L batch reactor equipped with a mechanical stirrer, reflux condenser, and thermometer under a nitrogen atmosphere. For example, in case of P23B$_{48}$CT (Table 2-1), DMT (188 g, 1.0 mol), 2,3-BD (140 g, 1.55
mol), CHDM (70 g, 0.5 mol), GeO₂ (150 ppm relatives to the total weight of monomers), and DBTO (300 ppm relatives to the total weight of monomers) were weighed into the reactor. The reaction mixture was heated from 180 °C to 230 °C over 3 h, and the temperature was maintained for 2 h until the end of the transesterification reaction. Methanol released at this stage was continuously removed by distillation. For the polycondensation reaction, the temperature was gradually increased to 245 °C or 260 °C, and the pressure was reduced to 2 mmHg for another 1 h to 4 h until the viscosity reached a maximum. In the polymerization of PE₆₉CT, the reaction time was adjusted to obtain a similar viscosity as the case of P12P₆₉CT to produce a similar molecular weight. After polymerization, the reaction pressure reduced to atmospheric condition using nitrogen. The mixture was poured into a water bath, and the quenched product was dried in a vacuum oven for 15 h at 60 °C.

**PE₆₉CT copolyesters.** ¹H NMR (600MHz; CDCl₃/TFA; Me₄Si): δ (ppm) 8.11 (4H, ArH), 4.71 (4H, OCH₂CH₂), 4.31 (4H, OCH₂CH (cis)), 4.20 (4H, OCH₂CH (trans)), 2.0~1.1 (10H, cyclohexane ring). ¹³C NMR (150MHz; CDCl₃/TFA; Me₄Si): δ (ppm) 165.9-165.5 (C=O), 134.6-133.6 (ArC), 129.9-129.6 (ArC), 70.3 (OCH₂CH₂), 68.2 (OCH₂CH (trans)), 21
63.2\((\text{OCH}_2\text{CH (cis)})\), 37~25 (cyclohexane ring).

**P12P, CT copolyesters.** \(^1\)H NMR (600MHz; CDCl\(_3\)/TFA; Me\(_4\)Si): \(\delta\) (ppm) 8.10 (4H, \(\text{ArH}\)), 5.56 (1H, OCH\(_2\text{CH}\)), 4.53 (2H, OCH\(_2\text{CH}\)), 4.29 (4H, OCH\(_2\text{CH (cis)}\)), 4.18 (4H, OCH\(_2\text{CH (trans)}\)), 2.1~1.1 (10H, cyclohexane ring), 1.49 (3H, CHCH\(_3\)). \(^{13}\)C NMR (150MHz; CDCl\(_3\)/TFA; Me\(_4\)Si): \(\delta\) (ppm) 166.0-159.2 (C=O), 134.6-133.6 (ArC), 129.8-129.7 (ArC), 70.4 (OCH\(_2\text{CH (trans)}\)), 69.5 (OCH\(_3\text{CH}\)), 68.2 (OCH\(_2\text{CH (cis)}\)), 67.1 (OCH\(_2\text{CH}\)), 37~25 (cyclohexane ring), 16.8 (CHCH\(_3\)).

**P23B, CT copolyesters.** \(^1\)H NMR (600MHz; CDCl\(_3\)/TFA; Me\(_4\)Si): \(\delta\) (ppm) 8.11 (4H, \(\text{ArH}\)), 4.71 (2H, OCHCH), 4.31 (4H, OCH\(_2\text{CH (cis)}\)), 4.20 (4H, OCH\(_2\text{CH (trans)}\)), 2.0~1.1 (10H, cyclohexane ring), 1.46 (6H, CHCH\(_3\)). \(^{13}\)C NMR (150MHz; CDCl\(_3\)/TFA; Me\(_4\)Si): \(\delta\) (ppm) 166.0-159.1 (C=O), 134.4-133.9 (ArC), 130.2-129.7 (ArC), 72.9 (OCHCH), 70.3 (OCH\(_2\text{CH (trans)}\)), 68.2 (OCH\(_2\text{CH (cis)}\)), 37~25 (cyclohexane ring), 16.4-15.4 (CHCH\(_3\)).

**2.2.3. Synthesis of the homopolyester**

To assign \(^{13}\)C NMR peaks for sequence distribution analysis,
homopolyester P12PT was synthesized on a small scale using a Kugelrohr oven. DMT (777 mg, 4 mmol), 1,2-PD (761 mg, 10 mmol), and DBTO (2.5 mg, 0.01 mmol) were weighed into a 10 mL round-bottom flask located inside the oven. The oven was heated from 160 °C to 200 °C over 3 h, and the reaction was continued at this temperature for 2 h to complete the transesterification reaction under a continuous flow of nitrogen. The temperature was then increased to 230 °C, and the vacuum of 10-20 mmHg was applied for another 3 h. After polymerization, the reaction condition was returned to atmospheric pressure using nitrogen, and the resulting polymer melt was cooled down. The product was dissolved in chloroform, precipitated into methanol and dried in vacuo after filtration.

**P12PT homopolyester.** $^1$H NMR (600MHz; CDCl$_3$/TFA; Me$_4$Si): δ (ppm) 8.06 (4H, $Ar\text{H}$), 5.55 (1H, OCH$_2$CH), 4.53 (2H, OCH$_2$CH), 1.48 (3H, CHCH$_3$). $^{13}$C NMR (150MHz; CDCl$_3$/TFA; Me$_4$Si): δ (ppm) 166.3-165.2 (C=O), 134.5-133.6 (ArC), 130.2-129.8 (ArC), 69.6 (OCH$_2$CH), 67.1 (OCH$_2$CH), 16.8 (CHCH$_3$). GPC: $M_n = 6835$, $M_w = 13\ 219$, PDI = 1.93
2.2.4. Characterization

*Intrinsic viscosity.* The intrinsic viscosity of the polyesters was measured using an automated Ubbelohde viscometer (SKYVIS) at 30 °C. Polymer samples (0.60 g) were weighed and dissolved in 30 mL of *o*-chlorophenol. This solution was heated at 150 °C for 15 min and stirred with a magnetic stir bar to ensure complete dissolution. Each solution was then cooled to room temperature. Intrinsic viscosity values were calculated from relative viscosities.

*Size Exclusion Chromatography (SEC).* The number and weight average of molecular weight, as well as molecular weight distribution, were determined by gel permeation chromatography (GPC) at 40 °C with Tosoh equipment provided with a refraction-index detector. Polymer samples (0.03 g) were carefully weighed and dissolved in 3 mL of *o*-chlorophenol at 150 °C for 15 min then added 9 mL of chloroform. The samples were chromatographed with a mixture solution of *o*-chlorophenol and chloroform (1:3, v/v) as a mobile phase using two Shodex LF804 columns at a velocity of 0.7 mL min\(^{-1}\). Chromatograms were calibrated against monodisperse polystyrene standards.
Density. Densities of the copolyesters were measured based on Archimedes’ principle using an AND GR 200 balance equipped with an AD-1653 density determination kit. Quenched polymer samples without bubbles were weighted.

Nuclear Magnetic Resonance (NMR). $^1$H and $^{13}$C NMR spectra were obtained using a JEOL ECA-600 spectrometer operating at 600 and 150 MHz, respectively, with either CDCl$_3$ or a CDCl$_3$:TFA-$d$ mixture (19:1, v/v) as the solvent. Tetramethylsilane (TMS) was used as an internal standard and as a reference for the chemical shifts. Sixteen scans with 16K data points each were acquired for each $^1$H NMR spectrum. Relaxation delays were 5 s. $^{13}$C NMR spectra were recorded at 150 MHz using the same NMR spectrometer and solvent mixture. Each $^{13}$C NMR spectrum was composed of 8192 scans with 64K data points each. Relaxation delays were 2 s.

Differential scanning calorimetry (DSC). DSC measurements were performed on a Mettler-Toledo DSC 820 calorimeter. Indium and zinc were used as a standard for temperature and enthalpy calibration. Pellet samples of about 10 mg were enclosed in standard 40 μL aluminum cells. The samples were melted at 300 °C for 5 min and then
quenched to 30 °C at a rate of 300 °C min\(^{-1}\). The temperature was then increased at a rate of 10 °C min\(^{-1}\) from 30 to 300 °C, under a nitrogen atmosphere. The \(T_g\) was estimated from the second heating line at the temperature of the inflection point of the shift in the baseline. The crystallization temperature (\(T_c\)) and melting temperature (\(T_m\)) were taken at the maximum of the respective exothermic and endothermic peak appearing on the second heating trace.

**Thermogravimetric analysis (TGA).** TGA was performed using a Perkin-Elmer TGA 7 with vertical balance instruments from 30 °C to 600 °C at a scan rate 10 °C min\(^{-1}\) under a nitrogen atmosphere. Sample weights of about 20 mg were used in these experiments.

**Wide-angle X-ray diffraction (WAXD).** The samples annealed at 160 °C for 24 h were used for WAXD analysis. The patterns were collected using a Bruker New D8 Advance diffractometer (Cu Kα radiation, \(\lambda = 0.1542 \text{ nm}\)) in the angular range of 10°–30° (\(2\theta\)). The degree of crystallinity (\(X_c\)) was calculated as the ratio between the peak areas corresponding to crystalline and amorphous components.
Tensile properties. The tensile properties were measured using an INSTRON 4465 testing machine at a strain rate of 5 mm min$^{-1}$ at room temperature. According to ISO 527-2, dumbbell-shaped specimens (1 BB type; 2 mm in thickness and 2 mm in width) were prepared using a BABYPLAST injection molding machine. Each tensile test was repeated at least five times, and the reported result was the average value obtained from measurements of at least three specimens excluding the minimum and maximum value. Descriptive statistics including the mean and standard deviation values were calculated for each test group. Student’s $t$-test: for two-group assuming equal variance, $P$ values of < 0.05 was chosen to determine if there was a significant difference between the two copolyesters samples. All statistical analyses were performed using Excel 2013 (Microsoft Corporation, Redmond, WA, USA).
2.3. Results and Discussion

2.3.1. Synthesis and characterization of PECT, P12PCT, and P23BCT copolyester

The copolyesters were synthesized through a two-step growth polycondensation reaction between DMT, CHDM and potentially biobased ethylene diols such as EG, 1,2-PD or 2,3-BD. The reaction scheme is shown in Scheme 2-1. The temperature was set at 180 °C for 3 h to prevent volatilization of the diols and then increased to 230 °C to avoid crystallization of the oligomers. Polycondensation reaction was conducted at 245 °C or 260 °C for 2 h under vacuum to remove the volatile by-products. Germanium oxide and DBTO were used as catalysts to obtain high molecular weight polymers.\[44, 56\] Three copolyester series, PECT, P12PCT, and P23BCT, were prepared, and the copolymerization results are summarized in Table 2-1. Copolyesters with ethylene diol and CHDM at molar ratios varying from 115/85 to 170/30 were prepared using a feed molar ratio of DMT to the total of diols of 1:2, and an excess of diol was ethylene diol, which has a lower boiling point than CHDM.

Copolymerization of DMT, CHDM, and EG produced PECT with
Scheme 2-1. Polymerization reaction leading to PECT, P12PCT, and P23BCT copolyesters.
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<td>P12P&lt;sub&gt;49&lt;/sub&gt;CT</td>
<td>150/50</td>
<td>48.7/51.3</td>
<td>12 900</td>
<td>27 600</td>
<td>2.14</td>
</tr>
<tr>
<td>8</td>
<td>P12P&lt;sub&gt;69&lt;/sub&gt;CT</td>
<td>170/30</td>
<td>69.3/30.7</td>
<td>10 900</td>
<td>26 700</td>
<td>2.44</td>
</tr>
<tr>
<td><strong>2,3-Butanediol (2,3-BD)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>P23B&lt;sub&gt;19&lt;/sub&gt;CT</td>
<td>115/85</td>
<td>18.5/81.5</td>
<td>21 000</td>
<td>47 800</td>
<td>2.28</td>
</tr>
<tr>
<td>10</td>
<td>P23B&lt;sub&gt;29&lt;/sub&gt;CT</td>
<td>130/70</td>
<td>29.4/70.6</td>
<td>17 500</td>
<td>48 700</td>
<td>2.78</td>
</tr>
<tr>
<td>11</td>
<td>P23B&lt;sub&gt;48&lt;/sub&gt;CT</td>
<td>150/50</td>
<td>48.1/51.9</td>
<td>13 200</td>
<td>30 900</td>
<td>2.35</td>
</tr>
<tr>
<td>12</td>
<td>P23B&lt;sub&gt;65&lt;/sub&gt;CT</td>
<td>170/30</td>
<td>64.9/35.1</td>
<td>6 800</td>
<td>11 400</td>
<td>2.25</td>
</tr>
</tbody>
</table>

<sup>a</sup>Molar ratio in the initial feed. The excess of diol with respect to DMT was in all cases achieved with ethylene diol (i.e., EG, 1,2-PD or 2,3-BD).  
<sup>b</sup>Molar composition determined by integration of the <sup>1</sup>H NMR spectra.  
<sup>c</sup>M<sub>n</sub>: number average molecular weight in g mol<sup>-1</sup>.  
<sup>d</sup>M<sub>w</sub>: weight average molecular weight in g mol<sup>-1</sup>.  
<sup>e</sup>PDI: polydispersity index.  
<sup>f</sup>Intrinsic viscosity in dL g<sup>-1</sup> measured in o-chlorophenol at 30 °C.  
<sup>g</sup>Density in g mL<sup>-1</sup>.
intrinsic viscosities between 0.4 and 0.8 dL g\(^{-1}\), and a number-average molecular weight ranged from 12,900 to 28,000 g mol\(^{-1}\). In the case of P12PCT and P23BCT copolyesters with 1,2-PD or 2,3-BD relatively low molecular weight copolymers were synthesized with intrinsic viscosities of 0.3 - 0.8 dL g\(^{-1}\) or 0.2 - 0.6 dL g\(^{-1}\) and number-average molecular weights of 11,000 – 26,000 g mol\(^{-1}\) or 6,800 – 21,000 g mol\(^{-1}\), respectively. The possible reason for the lower molecular weights compared with PECT under the same polymerization conditions stems from the lower reactivity of the secondary hydroxyl group of 1,2-PD or 2,3-BD than with that of the primary groups in EG. In order to minimize the effect of molecular weight, the reaction time of PE\(_{69}\)CT was adjusted to obtain a similar molecular weight to P12P\(_{69}\)CT. Although the molecular weights of copolyesters are different over a wide range, most copolyesters except P23B\(_{65}\)CT had acceptable \(M_n\) over 10,000; for the comparison of composition-dependent thermophysical properties of the copolymers\(^{[59]}\).

The densities of the copolyesters were measured based on Archimedes’ principle using a balance. The results are summarized in Table 2-1, and the dependence of density on CHDM contents is depicted in Fig. 2-1. The densities for amorphous PE\(_{34}\)CT and PE\(_{69}\)CT are 1.23 and 1.28 g mL\(^{-1}\), respectively, which are in good agreement with the reported
Fig. 2-1. Density of PECT (diamonds), P12PCT (squares), and P23BCT (triangles) copolyesters.
values.\(^{60,61}\) As shown in Fig. 2-1, the density of the polymers decreases with the content of CHDM for all three types of copolyesters and the slope decreases in the order of PECT, P12PCT, and P23BCT, which is in complete agreement with the order of increasing volumes of the diol comonomers, EG, 1,2-PD, and 2,3-BD, in the copolymers.

### 2.3.2. Structure analysis

The chemical structure and composition of P12PCT and P23BCT copolyester samples were analyzed by 1D and 2D NMR spectroscopy and compared with those of previously reported PECT\(^{62}\). Detailed NMR assignments are listed in the experimental section. Representative \(^1\)H and \(^{13}\)C NMR spectra of PECT, P12PCT, and P23BCT are shown in Fig. 2-2 with peak assignments. The assignment of the signals arising from the methyl group on the ethylene unit was supported by 2D NMR spectra, correlation spectroscopy (COSY), and heteronuclear single-quantum correlation spectroscopy (HSQC). Fig. 2-3 and Fig. 2-5 show the respective COSY spectra of P12P\(_{49}\)CT and P23B\(_{48}\)CT. The HSQC spectra of P12P\(_{49}\)CT and P23B\(_{48}\)CT are shown in Fig. 2-4 and Fig. 2-6, respectively. In the \(^{13}\)C NMR spectra of P23B\(_{48}\)CT, two methyl carbon
Fig. 2-2. (a) $^1$H-NMR and (b) $^{13}$C-NMR spectra of copolyesters of PECT, P12PCT, and P23BCT copolyesters.
Fig. 2-3. Correlation (COSY) spectra of P12P$_{49}$CT.
Fig. 2-4. Heteronuclear single-quantum correlation (HSQC) spectra of P12P_{49}CT.
Fig. 2-5. Correlation (COSY) spectra of P23B_{48}CT.
Fig. 2-6. Heteronuclear single-quantum correlation (HSQC) spectra of P23B$_{48}$CT.
peaks from respective isomeric *meso* and enantiomer structures (8 and 8′) appeared at 15.4 and 16.4 ppm, which was confirmed by HSQC.

The compositions of each copolyester were determined through quantification of the proton signals in $^1$H NMR spectra. The peak of the EG moiety in the PECT at δ 4.71 ppm was assigned to hydrogen atoms 7 and those of CHDM at δ 4.31, 4.20, and 2.0 ~ 1.1 ppm were assigned to hydrogen atoms 1(cis), 1(trans) and a cyclohexane ring, respectively. While the peaks of the 1,2-PD moiety in the P12PCT at δ 5.56, 4.53, 4.29, and 1.49 ppm were assigned to hydrogen atoms 7′, 7, 8, and 8′, respectively and the peaks of the 2,3-BD moiety in the P23BCT at δ 4.71 and 1.46 ppm were respectively assigned to hydrogen atoms 7 and 8. Quantification of the proton signals that arose from the oxymethylene (7) of the diol and the oxymethylene (1) of CHDM (sum of *trans* and *cis*) afforded their composition, which appeared to closely match those of their respective feeds, providing that all excess of ethylene diol was removed during the polycondensation reaction (Table 2-1).

The microstructures of the copolyesters were determined by $^{13}$C NMR. Two non-protonated aromatic carbons with chemical shifts of around 134 ppm are more sensitive to the sequence compared with any other carbon atoms, resulting from the through-space and through-bond
interactions between neighboring monomers. As shown in Fig. 2-7(a), there exist three possible dyad sequences, diol/TPA/diol (DTD; ETE, PTP or BTB), diol/TPA/CHDM (DTC; ETC, PTC or BTC), and CHDM/TPA/CHDM (CTC) where T, E, P, B, and C represent TPA, CHDM, 1,2-PD, 2,3-BD, and CHDM; the non-protonated carbons of TPA split into the peaks corresponding to these sequences. Sequence analysis of PECT and P23BCT was performed according to previous studies. The carbon resonances of P23BCT split into four peaks, similarly to PECT, allowing for precise analysis and assignment. In the case of P12PCT, 1,2-PD is asymmetric in contrast to EG and 2,3-BD; therefore the peak splitting pattern becomes more complicated because of the distinguishable sequence of primary or secondary hydroxyl groups. To analyze the exact peaks, the P12PT homopolyester was synthesized, and each peak was assigned as a control, as shown in Fig. 2-7(b). The number average sequence length (L) and degree of randomness (R) of the dyad were calculated using the following equations (Eq. (2-1) through (2-3)).
Fig. 2-7. (a) The three possible dyads occurring in PECT, P12PCT, and P23BCT copolyesters. (b) The non-protonated aromatic carbon region in the $^{13}$C NMR spectra of the copolyesters. (c) The plot of dyad contents vs. copolyester compositions. Dashed lines represent the theoretically calculated contents for random copolyesters.
\[ L_{DT} = \left( f_{DTD} + \left( \frac{f_{DTC}}{2} \right) \right) / \left( \frac{f_{DTC}}{2} \right) \]  \hspace{1cm} (2-1) \\
\[ L_{CT} = \left( f_{CTC} + \left( \frac{f_{DTC}}{2} \right) \right) / \left( \frac{f_{DTC}}{2} \right) \]  \hspace{1cm} (2-2) \\
\[ R = \left( \frac{1}{L_{DT}} \right) + \left( \frac{1}{L_{CT}} \right) \]  \hspace{1cm} (2-3) 

In these equations, \( L_{DT} \) and \( L_{CT} \) represent the average length of the ethylene diol (EG, 1,2-PD, or 2,3-BD) and CHDM units, respectively, and \( f_{DTD} \), \( f_{DTC} \), and \( f_{CTC} \) correspond to the fractions of the integrated intensities for each dyad configuration, as shown in Fig. 2-7(a) and (b).

Table 2-2 summarizes the theoretical and experimental values of \( L \) and \( R \) for the copolyesters. In the PECT and P12PCT copolyesters, the sequence distribution was essentially random over the entire range of compositions, with values of \( R \) being very close to 1, confirming that the structural unit distribution obeys Bernoullian statistics. When \( R < 1 \), the chain tends to form blocks of each unit, with \( R = 0 \) in a homopolymer mixture. If \( R > 1 \) the block length becomes shorter and a value of \( R = 2 \) indicates an alternating copolymer.\[64\]

Remarkably, in the case of P23BCT, with an increase of as the 2,3-BD contents, the sequence length (\( L_{DT} \)) of 2,3-BD initially increased
Table 2-2. Microstructure of PECT, P12PCT and P23BCT copolyesters.

<table>
<thead>
<tr>
<th>Copolyesters</th>
<th>Dyads fraction&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sequence length</th>
<th>Randomness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_{DTD}$</td>
<td>$f_{DTC}$</td>
<td>$f_{CTC}$</td>
</tr>
<tr>
<td>PECT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PE&lt;sub&gt;22&lt;/sub&gt;CT</td>
<td>4.4 (4.8)</td>
<td>34.9 (34.1)</td>
<td>60.8 (61.2)</td>
</tr>
<tr>
<td>PE&lt;sub&gt;34&lt;/sub&gt;CT</td>
<td>11.7 (11.5)</td>
<td>44.6 (44.8)</td>
<td>43.7 (43.7)</td>
</tr>
<tr>
<td>PE&lt;sub&gt;43&lt;/sub&gt;CT</td>
<td>28.9 (28.0)</td>
<td>50.0 (49.8)</td>
<td>21.2 (22.2)</td>
</tr>
<tr>
<td>PE&lt;sub&gt;69&lt;/sub&gt;CT</td>
<td>48.4 (47.2)</td>
<td>41.8 (43.0)</td>
<td>9.8 (9.8)</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;20&lt;/sub&gt;CT</td>
<td>1.8 (3.9)</td>
<td>30.2 (31.6)</td>
<td>68.1 (64.5)</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;31&lt;/sub&gt;CT</td>
<td>8.7 (9.8)</td>
<td>41.7 (43.0)</td>
<td>49.6 (47.2)</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;49&lt;/sub&gt;CT</td>
<td>26.9 (23.7)</td>
<td>49.5 (50.0)</td>
<td>23.7 (26.3)</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;69&lt;/sub&gt;CT</td>
<td>50.1 (48.0)</td>
<td>40.1 (42.6)</td>
<td>9.8 (9.4)</td>
</tr>
<tr>
<td>P23B&lt;sub&gt;19&lt;/sub&gt;CT</td>
<td>2.7 (3.0)</td>
<td>27.3 (28.5)</td>
<td>70.0 (68.6)</td>
</tr>
<tr>
<td>P23B&lt;sub&gt;29&lt;/sub&gt;CT</td>
<td>5.9 (8.6)</td>
<td>36.0 (41.5)</td>
<td>58.1 (49.8)</td>
</tr>
<tr>
<td>P23B&lt;sub&gt;48&lt;/sub&gt;CT</td>
<td>9.0 (23.1)</td>
<td>46.8 (49.9)</td>
<td>44.2 (26.9)</td>
</tr>
<tr>
<td>P23B&lt;sub&gt;65&lt;/sub&gt;CT</td>
<td>10.8 (42.1)</td>
<td>51.4 (45.6)</td>
<td>37.8 (12.3)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Experimental values were obtained by the equations mentioned in the text using the $^{13}$C NMR data. Theoretical values (in parentheses) were calculated on the basis of a statistical distribution using the compositional data given in Table 2-1.
maintaining randomness but converged to about 1.4, at which point it is no longer random as shown in Fig. 2-7 (c). This aberration can be explained by the different relativities of between the two monomers, CHDM and 2,3-BD. During the polycondensation reaction, highly reactive CHDM was incorporated into the chain through transesterification, and the less reactive and more volatile 2,3-BD is relegated to the end of the chain or eliminated as a by-product. As a result, $f_{DTD}$ became lower than the theoretical value, and conversely, $f_{DTC}$ and $f_{CTC}$ increased. Furthermore, these differences limited chain growth; leading to the difficulty to obtain high molecular weight polymer.

2.3.3. Thermal properties

Thermal transition behavior of the copolyesters was analyzed by DSC and the detailed data, $T_g$, $T_c$, $T_m$, and the corresponding enthalpies ($\Delta H_c$ and $\Delta H_m$), are listed in Table 2-3. A crystallization peak and a melting peak were found in the case of copolyesters with lower diol content, and the peak areas were smaller than for those with higher diol content. The variation in $T_g$ as a function of composition is plotted in Fig. 2-8. The $T_g$ of P12PCT copolyesters steadily decreased as 1,2-PD contents
Table 2-3. Thermal properties of PECT, P12PCT, and P23BCT copolyesters.

<table>
<thead>
<tr>
<th>Copolyesters</th>
<th>DSC&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ (°C)</td>
<td>$T_c$ (°C)</td>
</tr>
<tr>
<td>PE&lt;sub&gt;x&lt;/sub&gt;CT</td>
<td>85.9</td>
<td>158.3</td>
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<tr>
<td>PE&lt;sub&gt;22&lt;/sub&gt;CT</td>
<td>82.6</td>
<td>173.6</td>
</tr>
<tr>
<td>PE&lt;sub&gt;34&lt;/sub&gt;CT</td>
<td>80.9</td>
<td>-</td>
</tr>
<tr>
<td>PE&lt;sub&gt;53&lt;/sub&gt;CT</td>
<td>71.9</td>
<td>-</td>
</tr>
<tr>
<td>PE&lt;sub&gt;69&lt;/sub&gt;CT</td>
<td>71.9</td>
<td>-</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;x&lt;/sub&gt;CT</td>
<td>89.3</td>
<td>164.5</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;20&lt;/sub&gt;CT</td>
<td>87.4</td>
<td>185.1</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;31&lt;/sub&gt;CT</td>
<td>83.9</td>
<td>-</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;49&lt;/sub&gt;CT</td>
<td>83.3</td>
<td>-</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;69&lt;/sub&gt;CT</td>
<td>83.3</td>
<td>-</td>
</tr>
<tr>
<td>P23B&lt;sub&gt;x&lt;/sub&gt;CT</td>
<td>93.2</td>
<td>162.3</td>
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<td>P23B&lt;sub&gt;19&lt;/sub&gt;CT</td>
<td>93.4</td>
<td>191.2</td>
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<tr>
<td>P23B&lt;sub&gt;29&lt;/sub&gt;CT</td>
<td>94.5</td>
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<td>P23B&lt;sub&gt;48&lt;/sub&gt;CT</td>
<td>95.6</td>
<td>-</td>
</tr>
<tr>
<td>P23B&lt;sub&gt;65&lt;/sub&gt;CT</td>
<td>95.6</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>DSC data derived from the second heating run performed at a heating rate of 10 °C min<sup>-1</sup>. $T_g$ = Glass-transition temperature, $T_c$ = crystallization temperature, $\Delta H$ = enthalpy of transition, $T_m$ = melting temperature. <sup>b</sup>$T_{5\%}$ = Temperature at which a 5% of weight loss occurs. <sup>c</sup>$T_{max}$ = Temperature of the maximum rate of decomposition. <sup>d</sup>RW = Remaining weight at 600 °C.
Fig. 2-8. Glass transition temperature ($T_g$) of PECT (diamonds), P12PCT (squares), and P23BCT (triangles) copolyesters.
increased, which followed the same tendency for the case of PECT copolyesters, but the absolute value of $T_g$ at similar CHDM contents was higher than that of PECT. $T_g$ in P23BCT copolyesters increased with 2,3-BD content, and the difference with composition dramatically increased by 7.3 °C, 10.8 °C, 13.6 °C, and 23.7 °C compared with those in PECT of similar composition, even though P23BCT had lower molecular weight than PECT. These differences can be attributed to the increased number of methyl substituted groups in 2,3-BD, which resulted in the reduced chain flexibility. The methyl side groups produced an effect on enhancing the potential barriers to the rotation and the influence led to the increase of chain stiffness and $T_g$. The previous researches on polymethylmethacrylate (PMMA, $T_g \sim 115$ °C) – polymethylacrylate (PMA, $T_g \sim 14$ °C) and poly($\alpha$-methyl styrene) ($T_g \sim 168$ °C) – polystyrene ($T_g \sim 100$ °C) reported the same effect.\[65\] The negative slope of $T_g$ depending on the CHDM contents for the case of P23BCT in Fig. 2-8 supported the fact that 2,3-BD unit with higher chain stiffness contributed more to produce higher $T_g$ than CHDM did. The result was also supported by theoretical calculations of \textit{Molar Glass Transition Function}, $Y_g$, as shown in the Table S1-2 (Supporting Information).\[66\]
Thermal stability of the copolyesters was determined by TGA under a nitrogen atmosphere. Fig. 2-9 shows the TGA thermograms of the copolyesters. Table 2-3 summarizes the initial degradation temperature at 5 wt% loss of original weight (T_{5\%}), the temperature of maximum degradation rate (T_{max}), and the weight percentage of the residue at 600 °C. All copolyesters were thermally stable up to over 380 °C and displayed rapid decomposition between 420 °C and 480 °C, resulting in less than 1 % - 10 % residual remaining of the initial weight. The amount of residue from PECT decreases with increasing CHDM content, potentially due to reduced carbonization caused by the presence of cyclohexene ring or the lower oxygen content. The previous investigation with PETG reported similar results.\textsuperscript{[67]} In the case of P12PCT and P23BCT, the same trends as PECT were observed except P12P_{49}CT, but the remaining weight showed negligible differences. The PECT series has a higher decomposition temperature than that of the P12PCT or P23BCT series, probably due to the different bulkiness in structure, which led to the difference in packing efficiency between chains. In addition, the lateral methyl groups in P12PCT and P23BCT copolymers were more susceptible β-scission, which is known...
Fig. 2-9. TGA traces of PECT (a), P12PCT (b), and P23BCT (c) copolyesters recorded from 30 °C to 600 °C at 10 °C min⁻¹ under N₂ atmosphere.
as the main mechanism of polyester decomposition. The lower molecular weights also played a role in reducing the thermal stability; however, the $T_{\text{max}}$ for all copolyesters was over 400 °C, which was sufficiently high enough for general use in the plastics industry.

2.3.4. Crystallinity and mechanical properties

The powder WAXD patterns obtained from samples annealed at 160 °C for 24 h are compared in Fig. 2-10. Although PE$_{69}$CT and P12P$_{48}$CT exhibited slightly irregular patterns, other copolyesters with higher diol contents displayed broad amorphous patterns. PE$_{22}$CT, PE$_{34}$CT, P12P$_{20}$CT, P12P$_{31}$CT, P23B$_{19}$CT, and P23B$_{29}$CT were shown to be semicrystalline which supports the DSC results. Apparently, for either of the two copolyester series with 1,2-PD or 2,3-BD, similar diffraction peak positions are shared with PECT. All diffraction patterns exhibited five reflections at $2\theta$ of around 14.7° - 14.8°, 16.4° - 16.6°, 18.8° - 19.1°, 22.8° - 23.1°, and 25.2° - 25.5°, in complete agreement with previous literature for PECT$^{[67]}$. Crystallized copolyesters exhibited similar crystallinities, with $X_c$ of around 22.5 % ~ 25.7 %, and the detailed data are given in
Fig. 2-10. WAXD profiles of PECT (blue), P12PCT (red), and P23BCT (green) copolyesters annealed at 160 °C for 24 h.
Table 2-4. The results indicated that P12PCT and P23BCT copolyesters possessed the same crystal structure as PECT, suggesting that the effect of methyl side groups on the crystal structure was negligible.

<table>
<thead>
<tr>
<th>Copolyesters</th>
<th>Tensile Properties&lt;sup&gt;a&lt;/sup&gt;</th>
<th>WAXD&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Young’s Modulus (MPa)</td>
<td>Yield Strength (MPa)</td>
</tr>
<tr>
<td>PE&lt;sub&gt;x&lt;/sub&gt;CT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PE&lt;sub&gt;22&lt;/sub&gt;CT</td>
<td>940 ± 21</td>
<td>36.8 ± 0.5</td>
</tr>
<tr>
<td>PE&lt;sub&gt;34&lt;/sub&gt;CT</td>
<td>908 ± 17</td>
<td>37.1 ± 0.3</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;x&lt;/sub&gt;CT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P12P&lt;sub&gt;20&lt;/sub&gt;CT</td>
<td>939 ± 61</td>
<td>37.2 ± 0.2</td>
</tr>
<tr>
<td>P12P&lt;sub&gt;31&lt;/sub&gt;CT</td>
<td>1050 ± 16</td>
<td>39.2 ± 0.3</td>
</tr>
<tr>
<td>P23B&lt;sub&gt;x&lt;/sub&gt;CT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P23B&lt;sub&gt;19&lt;/sub&gt;CT</td>
<td>1077 ± 32</td>
<td>38.8 ± 0.1</td>
</tr>
<tr>
<td>P23B&lt;sub&gt;29&lt;/sub&gt;CT</td>
<td>1211 ± 15</td>
<td>40.3 ± 0.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Obtained from the tensile test at RT, averaged from tests performed at 5 mm/min with injection molded samples of 2 mm X 2 mm X 10mm.  
<sup>b</sup> The degree of crystallinity(X<sub>c</sub>) were measured with annealed samples at 160 °C for 24 h.
The stress-strain curves of the copolyesters are shown in Fig. 2-11, and the measured mechanical parameters are summarized in Table 2-4. Except for the PECT series, preparation of dumbbell-shaped specimens for the copolyesters containing high diol contents was limited probably due to the poor mechanical properties, stemmed from their low molecular weights. In each copolyester series, the yield strength decreased with the contents of cyclohexylene; this can be explained by the conformational transitions of the cyclohexylene ring, whose motions were found to be associated with the secondary relaxation of these copolymers.\textsuperscript{[58, 68]} As shown Fig. 2-12, although there is no difference between PE\textsubscript{22}CT and P12P\textsubscript{20}CT (P > 0.05), overall the copolymers with the higher amounts of lateral methyl groups displayed, the higher Young’s modulus and yield strength. These results can be supported by the fact that Young’s modulus is mainly determined by two parameters, molecular flexibility and interchain forces related to $T_g$.\textsuperscript{[69]} The previous reports comparing PMA and PMMA as well as PE and PP were in good agreement with the present results, where the only difference between the homopolymers is the presence of the methyl groups on the side groups of backbone chains. PMA and PE displayed a softer property than PMMA or PP, which supports that the absence of methyl
Fig. 2-11. Stress-strain curves of PECT (blue), P12PCT (red), and P23BCT (green) copolyesters.
Fig. 2-12. Young’s Modulus and Yield strength of PECT (diamonds), P12PCT (squares), and P23BCT (triangles) copolyesters.
groups on the side groups do not play a significant role in enhancing the intermolecular interactions between the polymeric chains. Instead, the bulkier PMMA or PP chains with methyl side groups experience a limited rotation of chains, which leads to a stiffer mechanical property. The backbone of present copolyesters consisted of relatively bulkier groups than that of polyacrylate or polyolefin, where the effect of the methyl group on the mechanical property was not so significant: however, a higher content of methyl-substituted diols resulted in increased stiffness of the obtained copolyesters. The modulus was also theoretically calculated by group contribution approach\textsuperscript{[66, 70]} and the calculation results supported these trend that the substituted methyl group made the polymer chain stiffer, as shown in the Table S2-2. (Supporting Information)
2.4. Conclusion

Two series of new copolyesters, P12PCT and P23BCT, were synthesized using 1,2-PD or 2,3-BD as a comonomer with CHDM and DMT. Increasing the molar ratio of ethylene diol in the feed made it challenging to obtain high molecular weight copolymers, probably due to the lower reactivity of the secondary hydroxyl group in the diol compounds. In case of P23BCT series, microstructure analysis using $^{13}$C NMR revealed that increasing the content of 2,3-BD in the copolymers reduced the degree of randomness and decreased the molecular weights because of the difference in reactivity between CHDM and 2,3-BD. When the ratio of copolymerized ethylene diol was lower than 30 mol %, copolyesters with high molecular weights around 17,500 – 21,000 g mol$^{-1}$ were synthesized. P12PCT and P23BCT copolyesters displayed lower densities, higher $T_g$, and stiffer mechanical properties compared with PECT with a similar ethylene diol content. The most notable effect resulting from the lateral methyl group was the outstanding increase in $T_g$, that is, the $T_g$ of P23B$_{48}$CT (94.5 °C) and P23B$_{65}$CT (95.6 °C) were noticeably higher than that of PE$_{53}$CT (80.9 °C) and PE$_{69}$CT (71.9 °C) despite its lower molecular weight. The thermal stability of the P12PCT and P23BCT copolyesters were in good agreement
with that of PECT, whose thermal stability decreased slightly with increasing the ethylene diol contents as a result of the instability of lateral methyl groups at a relatively high temperature. The P12PCT and P23BCT copolyesters were semi-crystalline or amorphous similar to PECT with the same crystalline structure. The Young’s modulus and yield strength increased with increasing the diol contents and the lateral methyl groups.
Chapter 3.

Copolyesters using 1,3-butandiol with 1,4-cyclohexanedicarboxylic acid and dimethyl terephthalate; Effect of different catalysts on molecular weight
3.1. Introduction

Biobased polymers have gained high interest in the last decades because of the increased concern about lack of fossil fuels and global warming.\textsuperscript{[20, 49, 71]} As mentioned previously (Section 1.2), polyesters are the most attractive among the various kind of polymer, because the monomers are readily accessible, and their unique and vast properties such as biodegradability and diverse application like packaging has accelerated the research and development of biobased polyesters.\textsuperscript{[24]}

Butanediol is one of a great number of chemicals developed as an alternative of petroleum-derived, especially biobased 1,4-BD is commercially produced by various companies and primarily used as a monomer of polyester (representatively, PBT and PBS) polyurethane and polyamide. 2,3-BD, which is one of another isomer, can be used as a precursor of a range of chemical products, including the solvents methyl ethyl ketone, gamma-butyrolactone, and 1,3-butadiene.\textsuperscript{[72]} Microbial production of 2,3-BD has been an object of research since the 1910s; many studies have improved strains, alternative fermentation substrates, improved cultivation techniques, downstream processing, and derivative production.\textsuperscript{[73]} Several attempts have been made to synthesize polyester with 2,3-BD as
reviewed previous chapter (Chapter 2.1).[54-56]

Although 1,3-BD is also an important chemical used for the production of polymers, antibiotics, pheromones, and insecticides,[74] researchers have not developed a bioprocess for the production of 1,3-BD using a renewable raw material, and no natural pathway exists.[75] 1,3-BD is produced through a multistep chemical reaction starting from acetaldehyde. Recently, several researchers constructed production routes of 1,3-BD using different microbial strains[76-78]. 1,3-BD can be used as a monomer of polyester; however, it is hard to find related research compared to 1,4-BD or 2,3-BD. Only as a plasticizer of polyvinylchloride or polylactic acid, low molecular weight polymer copolymerized with adipic acid were used.[79-81]

On the one hand, the catalyst is an important factor to obtain high molecular weight polyesters. Despite the importance, the mechanism of catalyst in the polycondensation reaction is poorly understood because the polycondensation process is difficult to analyze because of severe condition of polymerization (the high temperature and under vacuum).[82] And the research mainly focused on PET[83] such as antimony, germanium, and titanium for commercial use. Recently, there are several research results that polymerization for copolyester with various catalyst[56, 84-87], but almost all studies were limited to a simple screening test and did not explain the cause
of the different degree of polymerization.

In this study, polymerization of 1,3-BD with CHDM and DMT yielded a new polyester series, P13BCT. Notably, there is a difference of degree of polymerization and occurrence of side reaction depending on the catalyst, either DBTO or titanium (IV) butoxide (TBT). The product and by-products were analyzed, and mechanism of the reactions depending on catalysts was considered to identify the cause of the difference.

3.2. Experimental

3.2.1. Materials

DMT (99.9%), CHDM (99.8%) with 70 mol % of the trans isomer, germanium oxide (GeO₂), DBTO, and TBT were used as received from SK Chemicals (Korea). 1,3-BD (99.8%), and chloroform-\(d\) (99.8%) were purchased from Aldrich and used as received.

3.2.2. Synthesis of the copolyesters

P13BCT copolyesters were synthesized by melt polymerization in
two steps, transesterification and polycondensation. The copolyesters are called P13B_xCT with the subscripts x standing for their molar contents in 1,3-BD units. The corresponding monomers and catalysts were charged into a 1 L batch reactor equipped with a mechanical stirrer, reflux condenser, and thermometer under a nitrogen atmosphere. For example, in case of P13B_{52}CT (Table 3-1), DMT (188.4 g, 0.97 mol), 1,3-BD (135.5 g, 1.50 mol), CHDM (70.0 g, 0.49 mol), and TBT (250 ppm relatives to the total weight of monomers) were weighed into the reactor. The reaction mixture was heated from 180 °C to 220 °C over 3 h, and the temperature was maintained for 2 h until the end of the transesterification reaction. Methanol and other by-product released at this stage were continuously removed by distillation and sampled at regular interval for analysis. For the polycondensation reaction, the temperature was gradually increased to 235 °C, and the pressure was reduced to 2 mmHg for another 1 - 2 h until the viscosity reached a maximum. After polymerization, the reaction condition was returned to atmospheric pressure using nitrogen. The mixture was poured into a water bath, and the quenched product was dried in a vacuum oven for 15 h at 60 °C.
**P13B<sub>x</sub>CT copolyesters.** <sup>1</sup>H NMR (600MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ (ppm) 8.11 (4H, ArH), 5.41 (1H, OCH<sub>CH</sub>3), 4.71 (2H, OCH<sub>2</sub>CH<sub>2</sub>), 4.31 (4H, OCH<sub>2</sub>CH (cis)), 4.20 (4H, OCH<sub>2</sub>CH (trans)), 2.27 (2H, OCH<sub>2</sub>CH<sub>2</sub>), 2.0~1.1 (10H, cyclohexane ring), 1.46 (3H, OCHCH<sub>3</sub>). <sup>13</sup>C NMR (150MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ (ppm) 166.0-165.3 (C=O), 134.3-133.9 (ArC), 130.1-129.7 (ArC), 70.3 (OCH<sub>2</sub>CH (trans)), 69.4 (OCHCH<sub>3</sub>), 68.2 (OCH<sub>2</sub>CH (cis)), 62.0 (OCH<sub>2</sub>CH<sub>2</sub>), 34.8 (OCH<sub>2</sub>CH<sub>2</sub>), 37~25 (cyclohexane ring), 20.4 (CHCH<sub>3</sub>).

**P13B<sub>x</sub>CT_Sn copolyester with DBTO catalyst.** <sup>1</sup>H NMR (600MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ (ppm) 8.11 (4H, ArH), 5.8 (1H, CH<sub>2</sub>=CHCH<sub>2</sub>), 5.41 (1H, OCH<sub>CH</sub>3), 5.2~5.1 (2H, CH<sub>2</sub>=CHCH<sub>2</sub>), 4.5 (2H, OCH<sub>2</sub>CH<sub>2</sub>), 4.4 (2H, CHCH<sub>2</sub>CH<sub>2</sub>O), 4.31 (4H, OCH<sub>2</sub>CH (cis)), 4.20 (4H, OCH<sub>2</sub>CH (trans)), 2.6 (2H, CH<sub>2</sub>=CHCH<sub>2</sub>), 2.3 (2H, OCH<sub>2</sub>CH<sub>2</sub>), 2.0~1.1 (10H, cyclohexane ring), 1.46 (3H, OCHCH<sub>3</sub>). <sup>13</sup>C NMR (150MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ (ppm) 166.0-165.3 (C=O), 134.3-134.0 (ArC), 130.4 (CH<sub>2</sub>=CHCH<sub>2</sub>), 129.7 (ArC), 117.7 (CH<sub>2</sub>=CHCH<sub>2</sub>), 70.3 (OCH<sub>2</sub>CH (trans)), 69.4 (OCHCH<sub>3</sub>), 68.2 (OCH<sub>2</sub>CH (cis)), 64.6 (CHCH<sub>2</sub>CH<sub>2</sub>O), 62.0 (OCH<sub>2</sub>CH<sub>2</sub>), 34.8 (OCH<sub>2</sub>CH<sub>2</sub>), 33.3 (CH<sub>2</sub>=CHCH<sub>2</sub>), 37~25 (cyclohexane ring), 20.4 (CHCH<sub>3</sub>).
3.2.3. Characterization

The intrinsic viscosity, number and weight average of molecular weight, density, and $^1$H and $^{13}$C NMR spectra of samples were measured by the same methods described in section 2.2.2.

Gas Chromatography-Mass Spectrometry (GC-MS). The by-products were analyzed by GC-MS using an Agilent 6890-5973N equipped with a DB-WAX column (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm). The flow rate of helium carrier gas was 1.0 mL min$^{-1}$. Pyridine solutions containing 5 vol.% of the samples were injected into the injection port set at 250 °C with a split ratio of 30:1. The column was heated at 50 °C to 250 °C at a rate of 5 °C min$^{-1}$ and held for 5 min. The identification of all compounds was achieved using the NIST11 mass spectral data library. The quantification was done by area normalization method.

DSC and TGA measurements were performed the same way as described in section 2.2.2. The tensile properties were also measured the same methods described in section 2.2.2.
3.3. Results and Discussion

3.3.1. Synthesis and reaction mechanism of P13BCT copolyester

The copolyesters were synthesized through a two-step growth polycondensation reaction between DMT, CHDM and potentially biobased 1,3-BD. The reaction scheme is shown in Scheme 3-1. As shown Table 3-1, copolyesters with 1,3-BD and CHDM at molar ratios varying from 115/85 to 170/30 were prepared using a feed molar ratio of DMT to the total of diols of 1:2, and an excess of 1,3-BD, which has a lower boiling point than CHDM was added. The temperature was set at 180 °C for 3 h to prevent volatilization of the 1,3-BD and then increased to 220 °C to avoid crystallization of the oligomers. Polycondensation reaction was conducted at 235 °C for 2 h under vacuum to remove the volatile by-products. The copolymerization results for various molar ratios of diols are compared in Table 3-1, which provides the differences between DBTO and TBT catalyst. Although DBTO was known as an efficient catalyst to obtain high molecular weight polymer,[44, 56, 88] the resulting polyesters using DBTO attained extremely small molecular weight oligomers, with intrinsic viscosities around 0.1 dL g⁻¹ and M_n ranging from 2,000 g mol⁻¹ to 2,500 g mol⁻¹. On the other hand, when DBTO replaced by TBT catalyst, P13BCT with
Scheme 3-1. Polymerization reaction leading to P13BCT copolyesters.
Table 3-1. Composition and characteristics of the synthesized P13BCT copolyesters.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Code</th>
<th>Feed ratio&lt;sup&gt;a&lt;/sup&gt; CHDM/1,3-BD</th>
<th>Composition ratio&lt;sup&gt;b&lt;/sup&gt; CHDM/1,3-BD</th>
<th>Molecular weight&lt;sup&gt;d&lt;/sup&gt;</th>
<th>IV&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M&lt;sub&gt;n&lt;/sub&gt;</td>
<td>M&lt;sub&gt;w&lt;/sub&gt;</td>
</tr>
<tr>
<td>1</td>
<td>P13B&lt;sub&gt;21&lt;/sub&gt;CT_Sn</td>
<td>70/130</td>
<td>70.4/21.3/8.2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1 050</td>
<td>3 000</td>
</tr>
<tr>
<td>2</td>
<td>P13B&lt;sub&gt;37&lt;/sub&gt;CT_Sn</td>
<td>50/150</td>
<td>50.4/36.5/13.1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1 020</td>
<td>2 130</td>
</tr>
<tr>
<td>3</td>
<td>P13B&lt;sub&gt;57&lt;/sub&gt;CT_Sn</td>
<td>30/170</td>
<td>32.7/57.2/10.1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1 000</td>
<td>2 400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21 900</td>
<td>60 500</td>
</tr>
<tr>
<td>4</td>
<td>P13B&lt;sub&gt;29&lt;/sub&gt;CT</td>
<td>85/115</td>
<td>71.4/28.6</td>
<td>17 300</td>
<td>49 400</td>
</tr>
<tr>
<td>5</td>
<td>P13B&lt;sub&gt;38&lt;/sub&gt;CT</td>
<td>70/130</td>
<td>62.0/38.0</td>
<td>11 200</td>
<td>41 400</td>
</tr>
<tr>
<td>6</td>
<td>P13B&lt;sub&gt;52&lt;/sub&gt;CT</td>
<td>50/150</td>
<td>48.4/51.6</td>
<td>8 700</td>
<td>32 300</td>
</tr>
<tr>
<td>7</td>
<td>P13B&lt;sub&gt;69&lt;/sub&gt;CT</td>
<td>30/170</td>
<td>30.8/69.2</td>
<td>8 700</td>
<td>32 300</td>
</tr>
</tbody>
</table>

<sup>a</sup>Molar ratio in the initial feed. The excess of a diol concerning DMT was in all cases achieved with 1,3-BD.  
<sup>b</sup>Molar composition determined by integration of the <sup>1</sup>H-NMR spectra. <sup>c</sup>Molar ratio of vinyl end group.  
<sup>d</sup>M<sub>n</sub>: number average molecular weight in g mol<sup>−1</sup>, M<sub>w</sub>: weight average molecular weight in g mol<sup>−1</sup>. PDI: polydispersity index.  
<sup>e</sup>Intrinsic viscosity in dL g<sup>−1</sup> measured in o-chlorophenol at 30 °C.
intrinsic viscosities above 0.4 dL g\(^{-1}\) and \(M_n\) comprised in the 8,700 g mol\(^{-1}\) - 21,900 g mol\(^{-1}\) range were obtained.

To figure out the causes of the different results, the GC-MS analysis was carried out to identify the by-products collected by temperature during the transesterification reaction. As shown Fig. 3-2, in the case of DBTO catalyst, various unexpected by-product except methanol were detected on GC-MS, and their identifications are listed in Table 3-2. Especially the higher temperature, the more by-product of side reactions was detected. Probable reaction pathway from 1,3-BD to by-products was presented Scheme 3-2. Previous studies have reported similar reaction mechanism of 1,3-BD dehydration and oxidation in the vapor phase over solid acids such

Table 3-2. List of by-products during transesterification of P13B\(_{37}\)CT_Sn detected by GC-MS.

<table>
<thead>
<tr>
<th>No</th>
<th>RT(^a) (min)</th>
<th>Compound</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.55</td>
<td>3-Buten-2-one</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>2.13</td>
<td>2-Butenal</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>2.44</td>
<td>3-Buten-2-ol</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>3.64</td>
<td>3-Buten-1-ol</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>4.39</td>
<td>2-Buten-1-ol</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>4.38</td>
<td>2-Buten-1-ol, (Z)</td>
<td>72</td>
</tr>
</tbody>
</table>

\(^a\)RT: retention time
Fig. 3-1. GC-MS chromatograms of MeOH and other by-product solution during transesterification reaction of P13BCT_Sn (a) at 180 °C for initial 2 h, (b) at 200 °C following 2 h, (c) at 220 °C for the last 1 h.

Scheme 3-2. Probable reaction pathway from 1,3-BD to by-products over the tin catalyst.
as SiO$_2$-Al$_2$O$_3$, CeO$_2$-ZrO$_2$, and TiO$_2$ catalyst.$^{[89, 90]}$ Although the catalysts and reaction conditions are different, DBTO has oxide form like other catalysts in the previous research, and the reaction temperature of transesterification also seems high enough (over 200 °C) to occur these side reactions. Furthermore, as seen in the Fig. 3-1, except for methanol, the highest peak was the 3-butene-1-ol, this is in good agreement with the previous result. There are other researches$^{[91, 92]}$ about dehydration reaction of various diols with the CeO$_2$ catalyst. In these studies 1,3-diol such as 1,3-PD and 1,3-BD selectively dehydrated to allylic alcohol, whereas 1,2-PD and 2,3-BD hardly reacted. These results also explain why P12PCT and P23BCT were successfully polymerized with DBTO in the previous Chapter 2. As explained later, 3-butene-1-ol interrupt the growth of polymer chain as an end group.

On the one hand, TBT catalyst might be less active and acidic compared to the tin catalyst. Furthermore, TBT is composed of only alkoxide form so it would react different way compared to DBTO. It is well known the mechanism for catalyzed transesterification processes by dialkyntin derivatives$^{[93]}$ or titanium alkoxides$^{[94]}$, which is coordinative involving the formation of a complex between a carbonyl group and the metal atom. As shown Scheme 3-3, DBTO had to form tin alkoxide
Scheme 3-3. Mechanism of transesterification reaction with DBTO catalyst and 1,3-BD.
by reaction with alcohols (step 1) then transferred complexation of the carboxylic acid with the tin alkoxide followed by the insertion of the carboxylic group (step 2-1 or step 2-2). Otherwise, TBT is already oxide form, it directly coordinated with carbonyl group without reaction like step 1. There are two possible structures of tin alkoxide depending on hydroxyl group (1 and 2 in Scheme 3-3), the structure of these catalyst compounds are compared in Fig. 3-2. The tin alkoxide 2 is expected to exist at low concentration because of the low reactivity of secondary hydroxyl group, and the transesterification is hard to occur by steric hindrance as shown in Figure 3-2(c). Therefore, the step 2-1 is major for polycondensation and the end group of polymer chain would be mainly composed of the secondary hydroxyl group of 1,3-BD. The mechanism for the catalysts needs further study.

3.3.2. Structure analysis

The chemical structure and composition of P13BCT copolyester samples were analyzed by 1D and 2D NMR spectroscopy. Detailed NMR assignments are summarized in the experimental section. Representative $^1$H and $^{13}$C NMR spectra of P13BCT are shown in Fig. 3-3 and Fig. 3-4.
Fig. 3-2. Optimized geometries of (a) the TBT catalyst, (b) the tin alkoxide 1, and (c) the tin alkoxide 2 in the Scheme 3-3.
Fig. 3.3. $^1$H-NMR spectra of copolyesters of (a) P13B$_{37}$CT_Sn and (b) P13B$_{52}$CT copolyesters.
Fig. 3-4. $^{13}$C-NMR spectra of copolyesters of (a) P13B$_{37}$-Sn and (b) P13B$_{52}$CT.
with peak assignments. In case of a P13BCT with a tin catalyst, several unknown peaks originating from side-product were observed. Using 2D NMR spectra and NMR simulation software, the signals arising from the side-product were assigned as the vinyl end group generated from 3-butene-1-ol. Fig. 3-5 and Fig. 3-7 show the COSY spectra of P13B_{69}CT and P13B_{37}CT_Sn, respectively. The HSQC spectra of P13B_{69}CT and P13B_{37}CT_Sn are presented in Fig. 3-6 and Fig. 3-8, respectively.

The compositions of copolyester were determined through quantification of the proton signals in $^1$H NMR spectra. The peak of the 1,3-BD moiety in the P13BCT at δ 5.41, 4.71, 2.27, and 1.46 ppm were assigned to hydrogen atoms 7, 10, 9, and 8, respectively and those of CHDM at δ 4.31, 4.20, and 2.0 - 1.1 ppm were assigned to hydrogen atoms 1(cis), 1(trans) and a cyclohexane ring, respectively. The peak of vinyl group in the P13BCT with the tin catalyst at δ 5.8, 5.2 - 5.1, and 2.6 ppm were assigned to hydrogen atoms a, b, c, and d, respectively. Quantification of the proton signals that arise from the oxymethylene (7) of the 1,3-BD, the oxymethylene (1) of CHDM (sum of trans and cis), and the vinyl hydrogen (a) afforded their composition. CHDM remained almost same with feed ratio except for P13B_{29}CT and P13B_{38}CT, providing that all excess of 1,3-BD were removed during the
Fig. 3-5. Correlation (COSY) spectra of P13B\textsubscript{52}CT.
Fig. 3-6. Correlation (COSY) spectra of P13B\textsubscript{37}CT\_Sn
Fig. 3-7. Heteronuclear single-quantum correlation (HSQC) spectra of P13B_{52}CT.
Fig. 3-8. Heteronuclear single-quantum correlation (HSQC) spectra of P13B_{37}CT_{Sn}.
polycondensation reaction (Table 3-1). The content of vinyl end group of P13BCT with the tin catalyst is very high (8 - 13 mol%), this would be a significant cause of low molecular weight.

Pham et al.\cite{79} analyzed the end group of poly (1,3-butylene adipate), Reoplex® by $^1$H and $^{13}$C NMR. In this study, Reoplex® has similar molecular weight ($M_n = 1,950$, $M_w = 4,000$) with P13BCT_Sn and its chain-ends were made up of 28.6% of primary alcohol and 71.4 % of secondary alcohol, these peaks located at (1.7 - 1.8) ppm and (3.5 - 5.3) ppm regions of $^1$H resonances. However, no peak was observed in the regions in case of P13BCT_Sn; this proved that the end group of P13BCT_Sn was almost composed of the vinyl end group not hydroxyl group.

The microstructures of the copolyesters could be determined by $^{13}$C NMR using two non-protonated aromatic carbons, which are more sensitive to the sequence compared with any other carbon atoms, resulting from the through-space and through-bond interactions between neighboring monomers.\cite{63} As shown the dotted red box in Fig. 3-4, the non-protonated aromatic carbons with chemical shifts of around 134 ppm did not split enough to distinguish the dyad microstructure.
3.3.3. Densities and thermal properties

The densities of the copolyesters were measured based on Archimedes’ principle using a balance. The results are summarized in Table 3-3, and the density of P13BCT slightly increased with the content of 1,3-BD, which is in complete agreement with the relation of volumes between CHDM and 1,3-BD.

Thermal transition behavior of the copolyesters was analyzed by DSC and the detailed data, \(T_g\), \(T_c\), \(T_m\), and the corresponding enthalpies (\(\Delta H_c\), and \(\Delta H_m\)), are listed in Table 3-3. The \(T_g\) of P13BCT copolyesters steadily decreased as 1,3-BD contents increased from 74 °C to 51 °C due to the increase of chain flexibility. A crystallization peak and melting peak were found in case of P13B29CT and P13B38CT with lower 1,3-BD diol content, and the peaks were smaller as higher 1,3-BD content.

The evaluation of the thermal stability of the copolyesters was performed using TGA under a nitrogen atmosphere. Table 3-3 lists the initial degradation temperature at 5 wt% loss of original weight (\(T_{5\%}\)), the temperature of maximum degradation rate (\(T_{max}\)), and the weight percentage of the residue at 600 °C. All copolyesters show sufficient thermal stability; they were thermally stable up to over 330 °C and
Table 3-3. Densities and thermal properties of P13BCT copolyesters.

<table>
<thead>
<tr>
<th>Copolyesters</th>
<th>Density&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DSC&lt;sup&gt;b&lt;/sup&gt;</th>
<th>TGA&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_g$ (°C)</td>
<td>$T_c$ (°C)</td>
</tr>
<tr>
<td>P13B&lt;sub&gt;29&lt;/sub&gt;CT</td>
<td>1.19</td>
<td>74.1</td>
<td>145.4</td>
</tr>
<tr>
<td>P13B&lt;sub&gt;38&lt;/sub&gt;CT</td>
<td>1.20</td>
<td>68.2</td>
<td>155.1</td>
</tr>
<tr>
<td>P13B&lt;sub&gt;52&lt;/sub&gt;CT</td>
<td>1.21</td>
<td>59.8</td>
<td>-</td>
</tr>
<tr>
<td>P13B&lt;sub&gt;69&lt;/sub&gt;CT</td>
<td>1.22</td>
<td>50.6</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>Density in g mL<sup>-1</sup>.<sup>b</sup>DSC data derived from the second heating run performed at a heating rate of 10 °C min<sup>-1</sup>. $T_g$ = Glass-transition temperature, $T_c$ = crystallization temperature, $\Delta H$ = enthalpy of transition, $T_m$ = melting temperature. <sup>c</sup>$T_{5\%}$ = Temperature at which a 5% of weight loss occurs, $T_{\text{max}}$ = Temperature of the maximum rate of decomposition, RW = Remaining weight at 600 °C.
displayed rapid decomposition around 360 °C - 410 °C. Additionally, the residual weight left upon heating at 600 °C is about 5% - 8% of the initial weight. The decomposition temperature decreases with increasing 1,3-BD content, potentially due to the lateral methyl group of 1,3-BD and lower molecular weight. As mentioned previous chapter, the lateral methyl groups were more susceptible β-scission, which is known as the major mechanism of polyester decomposition\[51\]. Compared to P12PCT, the more alkylene unit (propylene not ethylene) also contribute the lower thermal stability.

### 3.3.4. Mechanical properties

The mechanical properties of the P13BCT copolyesters have been carried out by tensile testing with injection molded specimen. The measured mechanical parameters are presented in Table 3-4. In case of P13B\(_{69}\)CT, preparation of dumbbell-shaped specimens was limited probably due to the poor mechanical properties, stemmed from its low molecular weights. Although there was no statistical difference in Young’s modulus (P >0.05), the yield strength decreased with the contents of cyclohexylene; this can be explained by the conformational transition of
the cyclohexylene ring, whose motions were found to be associated with
the secondary relaxation of these copolymers.\textsuperscript{[58, 68]}

<table>
<thead>
<tr>
<th>Copolyesters</th>
<th>Tensile Properties$^a$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Young’s Modulus (MPa)</td>
<td>Yield Strength (MPa)</td>
</tr>
<tr>
<td>P13B\textsubscript{29}CT</td>
<td>1190 ± 17</td>
<td>39.4 ± 0.2</td>
</tr>
<tr>
<td>P13B\textsubscript{38}CT</td>
<td>1220 ± 62</td>
<td>42.3 ± 0.1</td>
</tr>
<tr>
<td>P13B\textsubscript{53}CT</td>
<td>1220 ± 41</td>
<td>43.6 ± 0.1</td>
</tr>
</tbody>
</table>

$^a$ Obtained from the tensile test at RT, averaged from tests performed at 5 mm/min with injection molded samples of 2 mm X 2 mm X 10mm.
3.4. Conclusion

Using 1,3-BD as a monomer with CHDM and DMT, the new copolyester, P13BCT, were synthesized. Depending on the type of catalyst, the results of the polymerization were significantly different. The side reaction occurred between 1,3-BD and DBTO catalyst, and the side-products were figured out by GC-MS and NMR analysis. Among them, 3-butene-1-ol was major and remained as a vinyl end group analysis restricting the growth of polymer chain. In the case of TBT catalyst, the P13BCT copolymers with high molecular weight were obtained. With increasing 1,3-BD content, high molecular weight polymers became difficult to obtain because of the lower reactivity of the secondary hydroxyl group. The density and yield strength slightly increased with increasing the 1,3-BD contents, whereas thermal stability, \( T_g \), and crystallinities decreased due to the increase of aliphatic carbon.
Chapter 4.

Synthesis and characterization of bio-based high $T_g$ copolyesters, P12PICT, and P12PIT using isosorbide and 1,2-propanediol
4.1. Introduction

ISB is one of the promising chemicals for biobased plastics because it is readily available from glucose and its rigid molecular structure could improve the heat-resistance of polymer, especially polyesters\textsuperscript{[19, 95, 96]}. The studies of polyester using ISB have been steadily increased and progressed\textsuperscript{[96, 97]}

In the early stage of studies before 2000, to overcome the low reactivity of ISB, almost polyesters were synthesized using dichloride acid instead of dicarboxylic acid. ISB reacted with various dichlorides such as terephthaloyl dichloride\textsuperscript{[98-101]}, FDCA dichloride\textsuperscript{[30]}, and aliphatic dicarboxylic acid dichlorides with different chain length\textsuperscript{[102, 103]}. The synthesized polyesters had high molecular weight enough to investigate the properties such as $T_g$, melting point, crystallinity, and degradability. However, most of the synthetic method of dichloride was solution polymerization using solvents such as toluene, pyridine, and Dimethyl sulfoxide; and hydrogen chloride was produced as a by-product, so it is not suitable for the commercial process.

Noordover et al.\textsuperscript{[53, 104]} synthesized copolyesters for powder coating application using isosorbide with succinic acid or citric acid through
conventional melt polymerization. However, the molecular weight relatively low \((M_n = 2000 - 4600 \text{ g mol}^{-1})\). Kricheldorf et al.\(^{[105]}\) compared two synthetic results of PIBT copolyester composed of DMT, ISB, and 1,4-BD between melt polymerization and solution polymerization with terephthaloyl chloride. They concluded that the melt polymerization method was not suited for syntheses of copolyesters with a high concentration of ISB because the composition of ISB compared to feed ratio and the molecular weight is relatively low due to low reactivity of ISB.

Many researchers tried to solve the problem with various methods. There are already successful examples of copolyesters using ISB with high molecular weight through melt polymerization. First, Bersot et al.\(^{[85]}\) synthesized poly(ethylene isosorbide terephthalate) (PEIT) using new bimetallic catalytic systems, which overcame the lack of reactivity of ISB and discoloration. For the synthesis of PEIT with 20 mol% of ISB content, they found optimized catalytic system (i.e., Sb:Al 1:0.25), however, the \(M_n\) was less than 10,000, which is not enough to evaluate thermophysical properties. Second, Yoon et al.\(^{[106]}\) synthesized poly(isosorbide 1,4-cyclohexane dicarboxylate) (PICD) of ISB and 1,4-cyclohexane dicarboxylic acid (CHDA), using catalyst systems with acetic anhydride \((\text{Ac}_2\text{O})\). Although they obtained a high-molecular-weight homopolyester
\( M_n = 12,000 \text{ - } 18,000 \ \text{g mol}^{-1} \), this method was ineffective for copolyesters. Similarly Feng et al.\(^{107, 108}\) designed new synthetic strategy using dimethyl carbonate, which could transform the secondary hydroxyl groups of ISB to a more reactive methyl carbonate group. The designed precursor, oligo(isosorbide carbonate), reacted with DMT or TPA and diol such as EG and 1,4-BD, as the results, high-molecular-weight poly(isosorbide carbonate) (PIC) or poly(isosorbide carbonate-co-butylene terephthalate)s (PICBTs) were synthesized.

However, these synthetic approaches are far from being commercialized especially concerning mass production. Another readily applicable way is to incorporate effective comonomer primary hydroxyl groups such as CHDM as already reviewed for copolyesters with ISB\(^{45}\), terpolyesters of EG, ISB with TPA\(^{44, 109, 110}\), and furan-based copolyesters\(^{46}\) (refer to Section 2.1).

On the one hand, 1,2-PD has plenty of potential and obvious advantage as a monomer of polyesters because it has good reactivity compared to 2,3-BD and the lateral methyl group could impart superior properties. Also, 1,2-PD is lower toxic than EG because it is converted to pyruvic acid and incorporated into the TCA cycle.\(^{18}\). However, as we reviewed in the previous chapter 2.1, studies on polyesters using 1,2-PD as
monomer has been limited. In this study, novel P12PICT copolyesters were synthesized by introducing 1,2-PD as comonomer instead of EG in PEICT. Additionally, by excluding CHDM, P12PIT with more biobased contents and higher \( T_g \) were polymerized.

4.2. Experimental

4.2.1. Materials

DMT (99.9%), EG (99.8%), ISB (99.9%), CHDM (99.8%) with 70 mol % of the trans isomer, germanium oxide (GeO\(_2\)), DBTO, and TBT were used as received from SK Chemicals (Korea). 1,2-PD (99.5%) and chloroform-\( d \) (99.8) were purchased from Aldrich and used as received.

4.2.2. Synthesis of the PEICT and P12PICT copolyesters

The two types of copolyesters, PEICT and P12PICT, were synthesized by melt polymerization in two steps, transesterification and polycondensation. These copolyesters are called PEI\(_x\)CT, and P12PI\(_x\)CT with the subscripts \( x \) standing for their molar contents in ISB units. The
corresponding monomers and catalysts were charged into a 1 L batch reactor equipped with a mechanical stirrer, reflux condenser, and thermometer under a nitrogen atmosphere. For example, in case of P12PI_{19}CT (Table 4-1), DMT (193.5 g, 1.00 mol), ISB (58.2 g, 0.40 mol), 1,2-PD (87.2 g, 1.15 mol), CHDM (65.5 g, 0.45 mol), GeO_2 (150 ppm relatives to the total weight of monomers), and DBTO (300 ppm relatives to the total weight of monomers) were weighed into the reactor. The reaction mixture was heated from 180 °C to 230 °C over 3 h, and the temperature was maintained for 2 h until the end of the transesterification reaction. Methanol released at this stage was continuously removed by distillation. For the polycondensation reaction, the temperature was gradually increased to 245 °C, and the pressure was reduced to 2 mmHg for about 30 min, then the reactor was heated to 250 °C for another 30 min to 150 min under vacuum until the viscosity reached a maximum. After polymerization, the reaction condition was returned to atmospheric pressure using nitrogen. The mixture was poured into a water bath, and the quenched product was dried in a vacuum oven for 15 h at 60 °C.
PEI<sub>x</sub>CT copolyesters. <sup>1</sup>H NMR (600MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ (ppm) 8.11 (4H, ArH-5), 5.51 (1H, H-6), 5.46 (1H, H-10), 5.01 (1H, H-8), 4.71 (5H, H-1,2,9), 4.30 (4H, CH-11 (cis)), 4.20 (4H, H-11 (trans)), 4.1 (2H, H-7,7”), 2.08 (2H, H-12 (cis)), 1.95 (4H, H-13a (trans)), 1.82 (4H, H-12 (trans)), 1.68 (4H, H-13a (cis)), 1.59 (4H, H-13b (cis)), 1.17 (4H, H-13b (trans)). 

<sup>13</sup>C NMR (150MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ (ppm) 166.0-164.9 (C<sub>3</sub>), 134.8-133.3 (C<sub>4</sub>), 130.0-129.7 (C<sub>5</sub>), 86.3 (C<sub>9</sub>), 81.3 (C<sub>8</sub>), 79.0 (C<sub>6</sub>), 75.1 (C<sub>10</sub>), 73.6 (C<sub>7</sub>), 70.9 (C<sub>7</sub>), 70.3 (C<sub>11</sub>(0)), 68.2 (C<sub>11</sub>(c)), 63.2 (C<sub>1</sub>, C<sub>2</sub>), 37.3 (C<sub>12</sub>(0)), 34.8 (C<sub>12</sub>(c)), 29.1 (C<sub>13</sub>(0)), 25.6 (C<sub>13</sub>(c)).

P12PI<sub>x</sub>CT copolyesters. <sup>1</sup>H NMR (600MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ (ppm) 8.11 (4H, ArH-5), 5.57 (1H, H-1), 5.51 (1H, H-6), 5.46 (1H, H-10), 5.09 (1H, H-8), 4.71 (1H, H-9), 4.5 (2H, H-2), 4.30 (4H, CH-11 (cis)), 4.19 (4H, H-11 (trans)), 4.09 (2H, H-7,7”), 2.07 (2H, H-12 (cis)), 1.95 (4H, H-13a (trans)), 1.82 (4H, H-12 (trans)), 1.68 (4H, H-13a (cis)), 1.58 (4H, H-13b (cis)), 1.50 (3H, H-14), 1.17 (4H, H-13b (trans)). <sup>13</sup>C NMR (150MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): δ (ppm) 166.0-164.9 (C<sub>3</sub>), 134.5-133.1 (C<sub>4</sub>), 129.8 (C<sub>5</sub>), 86.3 (C<sub>9</sub>), 81.3 (C<sub>8</sub>), 79.0 (C<sub>6</sub>), 75.1 (C<sub>10</sub>), 73.6 (C<sub>7</sub>), 71.0 (C<sub>7</sub>), 70.4 (C<sub>11</sub>(0)), 69.6 (C<sub>1</sub>), 68.2 (C<sub>11</sub>(c)), 67.1 (C<sub>2</sub>), 37.3 (C<sub>12</sub>(0)), 34.8 (C<sub>12</sub>(c)), 29.1 (C<sub>13</sub>(0)), 25.6 (C<sub>13</sub>(c)), 16.8 (C<sub>14</sub>).
4.2.3. **Synthesis of the P12PIT copolyesters**

The P12PIT copolyesters were synthesized by the similar procedure of P12PI\(_x\)CT described in the previous section, except CHDM and changing catalyst from DBTO to TBT. DMT (198.9 g, 1.02 mol), 1,2-PD (109.1 g, 1.43 mol), ISB (89.8 g, 0.62 mol), and TBT (200 ppm relative to the total weight of monomers) were weighed into the reactor at a molar ratio of DMT/Diol = 1/2 for P12PI\(_{41}\)T (Table 4-2). And other copolyesters were obtained differing for each composition feed.

**P12PI\(_x\)T copolyesters.** \(^1\)H NMR (600MHz; CDCl\(_3\); Me\(_4\)Si): \(\delta\) (ppm) 8.08 (4H, ArH-5), 5.56 (1H, H-1), 5.49 (1H, H-6), 5.40 (1H, H-10), 5.08 (1H, H-8), 4.70 (1H, H-9), 4.5 (2H, H-2), 4.09 (2H, H-7,7'), 1.49 (3H, H-11), 1.17 (4H, H-13b (trans)). \(^{13}\)C NMR (150MHz; CDCl\(_3\); Me\(_4\)Si): \(\delta\) (ppm) 165.5-164.9 (C\(_3\)), 134.5-133.4 (C\(_4\)), 129.8 (C\(_5\)), 86.3 (C\(_9\)), 81.3 (C\(_8\)), 79.0 (C\(_6\)), 75.1 (C\(_{10}\)), 73.5 (C\(_7\)), 70.9 (C\(_7^\prime\)), 69.6 (C\(_{11}\)), 67.1 (C\(_2\)), 16.8 (C\(_{11}\)).
4.2.4. Characterization

The intrinsic viscosity, number and weight average of molecular weight, density, and $^1$H and $^{13}$C NMR spectra of samples were measured by the same methods described in section 2.2.2. DSC and TGA measurements were also performed the same way as described in section 2.2.2. The tensile properties were measured by the same methods described in section 2.2.2 except the strain rate. In case of PEICT or P12PICT, the strain rate was same as previous condition (i.e., 5 mm min$^{-1}$), however, in case of P12PIT, the rate was modified to 1 mm min$^{-1}$ due to the brittleness of sample.
4.3. Results and Discussion

4.3.1. Synthesis and characterization of PEICT and P12PICT copolyesters

The synthesis of PEICT and P12PICT copolyesters was performed by a two-step growth polycondensation reaction between DMT, CHDM, biobased isosorbide, and EG or 1,2-PD respectively, as described in Scheme 4-1. The temperature was set at 200 °C for 3 h to prevent volatilization of the diols and then increased to 235 °C to avoid crystallization of the oligomers. Polycondensation reaction was conducted at 250 °C for 1 - 2 h under vacuum to remove the volatile by-products. Germanium oxide and DBTO were used as catalysts to obtain high molecular weight polymers\textsuperscript{[44, 56]} and the copolymerization results are summarized in Table 4-1.

Copolymerization of DMT, CHDM, ISB, and EG produced PEICT with intrinsic viscosities between 0.55 dL g\textsuperscript{-1} and 0.66 dL g\textsuperscript{-1}, and a number-average molecular weight ranged from 17,800 to 23,100 g mol\textsuperscript{-1}. In the case of copolymers were synthesized with intrinsic viscosities of (0.48 - 0.61) dL g\textsuperscript{-1} and number-average molecular weights of (11,900 – 19,600) g mol\textsuperscript{-1}. The possible reason for the lower molecular weights
Scheme 4-1. Reaction scheme for the polymerization of PEICT and P12PICT copolyesters
Table 4-1. Composition and molecular weight of the synthesized PEICT and P12PICT copolyesters.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Code</th>
<th>Feed ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Composition ratio&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Residual ISB&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>Molecular weight</th>
<th>IV&lt;sup&gt;g&lt;/sup&gt;</th>
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<td></td>
<td></td>
<td>Diol/ISB/CHDM</td>
<td>Diol/ISB/CHDM</td>
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<td>M&lt;sub&gt;n&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>M&lt;sub&gt;w&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt;</td>
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</tr>
<tr>
<td></td>
<td>Ethylene glycol (EG)</td>
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<td>22 300</td>
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<tr>
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<tr>
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<td>1,2-Propanediol (1,2-PD)</td>
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<td>46.3/7.0/46.7</td>
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<td>76 200</td>
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<td>19 100</td>
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<td>14.4/39.8/45.8</td>
<td>39.8</td>
<td>14 400</td>
<td>44 600</td>
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</tbody>
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<sup>a</sup>Molar ratio in the initial feed. The excess of diol with respect to DMT was in all cases achieved with ISB and EG or 1,2-PD.

<sup>b</sup>Molar composition determined by integration of the <sup>1</sup>H NMR spectra.

<sup>c</sup>Ratio feeding to the composition of ISB M<sub>n</sub>: number average molecular weight in g mol<sup>−1</sup>. M<sub>w</sub>: weight average molecular weight in g mol<sup>−1</sup>. PDI: polydispersity index. IV: Intrinsic viscosity in dL g<sup>−1</sup> measured in o-chlorophenol at 30 °C.
compared with PEICT under the same polymerization conditions stems from, the lower reactivity of the secondary hydroxyl group of 1,2-PD than with that of the primary groups in EG.

4.3.2. Synthesis and characterization of P12PIT copolyesters

To obtain copolyesters with more contents of renewable sources and higher $T_g$, P12PIT except CHDM were synthesized through similar polycondensation process differing catalyst and the scheme is shown in Scheme 4-2. As explained in Supporting Information, when DBTO catalyst was used, an undesirable side reaction occurred (Table S3-1). Similar to P13BCT synthesis case under tin catalyst, dehydration reaction of 1,2-PD occurred and the vinyl end group inhibit the chain growth (Fig. S3-1, refer to Supporting Information). The copolymerization results with TBT catalyst for various molar ratios of diols are summarized in Table 4-2. The resulting P12PIT polyesters had intrinsic viscosities 0.3 - 0.5 dL g$^{-1}$ and number-average molecular weights of 9,000–15,600 g mol$^{-1}$. Compared to P12PICT, P12PIT copolyesters have lower molecular weight due to the absence of reactive CHDM.
Scheme 4-2. Synthetic route of P12PIT copolyesters
Table 4-2. Composition and molecular weight of the synthesized P12PIT copolyesters.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Code</th>
<th>Feed ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Composition ratio&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Residual ISB&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>Molecular weight</th>
<th>IV&lt;sup&gt;g&lt;/sup&gt;</th>
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<td>51.9/48.1</td>
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<td>40.8/59.2</td>
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<td>16</td>
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<td>34.3/65.7</td>
<td>54.8</td>
<td>15 600</td>
<td>35 000</td>
</tr>
</tbody>
</table>

<sup>a</sup>Molar ratio in the initial feed.  
<sup>b</sup>Molar composition determined by integration of the <sup>1</sup>H NMR spectra.  
<sup>c</sup>Ratio feeding to the composition of ISB.  
<sup>d</sup>M<sub>n</sub>: number average molecular weight in g mol<sup>−1</sup>.  
<sup>e</sup>M<sub>w</sub>: weight average molecular weight in g mol<sup>−1</sup>.  
<sup>f</sup>PDI: polydispersity index.  
<sup>g</sup>Intrinsic viscosity in dL g<sup>−1</sup> measured in o-chlorophenol at 30 °C.
4.3.3. Structure and composition analysis

The chemical structure and composition of copolyester samples were analyzed by 1D and 2D NMR spectroscopy. Detailed NMR assignments are listed in the experimental section. Representative $^1$H and $^{13}$C NMR spectra of each copolyester for representative composition are shown in Fig. 4-1 and Fig. 4-2 with peak assignments. The peaks of PEICT spectra were good agreement with the previous literature\cite{44}. Fig. 4-3 displays the COSY spectrum of P12PI$_{25}$CT as representative identifying the existence of each moiety in units. The HSQC spectrum of P12PI$_{25}$CT is shown Fig. 4-4, which also confirm the correlation signals between proton and carbon of each moiety.

The compositions of copolyester were determined through quantification of the proton signals arising from the oxymethylene (2 of EG or 1,2-PD and 11 of CHDM (sum of $trans$ and $cis$)), oxymethine (6 and 10 of ISB) in $^1$H NMR spectra. In case of PEICT, the peak of the EG moiety at 4.7 ppm overlapped that of hydrogen atom 9 of the ISB moiety. CHDM remained almost same with feed, providing that all excess of volatile diols (EG or 1,2-PD) and unreacted ISB be removed during the polycondensation reaction (Table 4-1 and 4-2). As a result, the content of ISB in the feed was
Fig. 4-1. $^1$H-NMR spectra of copolyesters of (a) PEICT, (b) P12PICT, and (c) P12PIT copolyesters.
Fig. 4-2. $^{13}$C-NMR spectra of copolyesters of (a) PEICT, (b) P12PICT, and (c) P12PIT copolyesters.
Fig. 4-3. Correlation (COSY) spectra of P12PI$_{25}$CT.
Fig. 4-4. Heteronuclear single-quantum correlation (HSQC) spectra of P12PI25CT.
not totally incorporated into the polyester chain, and this fact is also known.\cite{97,111}

As shown Fig. 4-5, Table 4-1, and 4-2, the residual ratio of ISB varied depending on the composition of the copolyester. In case of PEICT, only 33% - 37% ISB of feed remained, however, 40% - 58% of ISB reacted in P12PICT. Furthermore, over 55% of ISB participated to polymerization in P12PIT, especially at lower ISB feed ratio, higher ISB remained. This may be caused by the lower reactivity of 1,2-PD compared to EG or CHDM; it was possible to synthesize P12PIT with higher ISB contents and higher $T_g$.

### 4.3.4. The microstructures and sequence distribution analysis

The microstructures of poly(alkylene terephthalate)s were usually analyzed using non-protonated aromatic carbons with chemical shifts of around 134 ppm.\cite{63,112} Because they are more sensitive to the sequence compared with any other carbon atoms, they split into each correspondence peaks with the sequence of through-space and through-bond interactions between neighboring monomers.

As shown in Fig. 4-6, PEICT or P12PICT copolyesters have six
Fig. 4-5. ISB feed ratio vs. ISB content of PEICT (squares), P12PICT (triangles), and P12PIT (diamonds) copolyesters.
Fig. 4-6. $^{13}$C NMR signals of various polyesters (a) P12PT, (b) PEICT, (c) P12PIT, (d) P12PCT, and (e) P12PICT (left) with indication of dyads for the microstructure analysis of copolyesters (right)
possible dyad sequences, CTI, DTC (ETC or PTC), DTI (ETI or PTI), CTC, DTD (ETE or PTP), and ITI where T, D, E, P, I, and C represent TPA, Diol, EG, 1,2-PD, ISB, and CHDM; the quaternary carbons of terephthalic units split into the peaks corresponding to these sequences. In the case of P12PIT copolyesters, there exist three possible dyad sequences except for CTI, PTC, and CTC. Sequence analysis of PEICT was performed according to previous studies\textsuperscript{[44, 109]} as shown in Fig. 4-6 (b). In the case of P12PICT, each peak was assigned refer to the spectra of a P12PT homopolymer, P12PCT, and P12PIT copolyesters. The spectra for each copolyester series, PEICT, P12PICT, and P12PIT are displayed in Fig. 4-7, Fig. 4-8, and Fig. 4-9, respectively. By integration of the peaks included in these signals, the molar fractions of dyads ($f_{\text{CTI}}$, $f_{\text{DTC}}$, $f_{\text{DTI}}$, $f_{\text{CTC}}$, $f_{\text{DTD}}$, and $f_{\text{ITI}}$) could be calculated. In case of PEICT and P12PICT, the number average sequence length (L) and degree of randomness (R) of the dyad were calculated using the following equations (Eq. (4-1) through (4-4))\textsuperscript{[63]}.

$$L_{DT} = \frac{f_{\text{DTD}} + \frac{f_{\text{DTC}} + f_{\text{DTI}}}{2}}{\frac{f_{\text{DTC}} + f_{\text{DTI}}}{2}} \quad (4-1)$$
Fig. 4-7. Extended $^{13}$C NMR spectra of PEICT terpolyester series; (a) PEI$_7$CT, (b) PEI$_{13}$CT, (c) PEI$_{21}$CT, and (d) PEI$_{29}$CT
Fig. 4-8. Extended $^{13}$C NMR spectra of P12PICT terpolyester series; (a) P12PI$_7$CT, (b) P12PI$_{12}$CT, (c) P12PI$_{19}$CT,
(d) P12PI$_{25}$CT, (e) P12PI$_{33}$CT, and (f) P12PI$_{40}$CT.
Fig. 4-9. Extended $^{13}$C NMR spectra of P12PIT copolyester series; (a) P12PI$_{15}$T, (b) P12PI$_{27}$T, (c) P12PI$_{41}$T, (d) P12PI$_{48}$T, (e) P12PI$_{59}$T, and (f) P12PI$_{66}$CT.
\[ L_{CT} = \frac{f_{CTC} + \left(\frac{f_{DTC} + f_{CTI}}{2}\right)}{\left(\frac{f_{DTC} + f_{CTI}}{2}\right)} \]  
(4 - 2)

\[ L_{IT} = \frac{f_{ITI} + \left(\frac{f_{DTI} + f_{CTI}}{2}\right)}{\left(\frac{f_{DTI} + f_{CTI}}{2}\right)} \]  
(4 - 3)

\[ R = \left(\frac{1}{L_{DT}}\right) + \left(\frac{1}{L_{CT}}\right) + \left(\frac{1}{L_{IT}}\right) - 1 \]  
(4 - 4)

In these equations, \( L_{DT} \), \( L_{CT} \), and \( L_{IT} \) represent the average length of the ethylene diol (EG, or 1,2-PD), CHDM, and ISB units, respectively. Table 4-3 summarizes the theoretical and experimental values of \( L \) and \( R \) for the copolyesters.

In case of P12PIT copolyesters, the values of \( L \) and \( R \) of the dyad were calculated using the following equations (Eq. (4-5) through (4-7))\(^{[63]}\).

\[ L_{PT} = \frac{f_{PTP} + \left(\frac{f_{PTC}}{2}\right)}{\left(\frac{f_{PTC}}{2}\right)} \]  
(4 - 5)

\[ L_{IT} = \frac{f_{ITI} + \left(\frac{f_{PTI}}{2}\right)}{\left(\frac{f_{PTI}}{2}\right)} \]  
(4 - 6)
Table 4-3. Microstructure of PEICT and P12PICT copolyesters.

<table>
<thead>
<tr>
<th>Copolyesters</th>
<th>Composition (Diol/ISB/CHDM)</th>
<th>Dyads fraction$^a$</th>
<th>Sequence length</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$f_{CT}$</td>
<td>$f_{DTC}$</td>
<td>$f_{DTI}$</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;1&lt;/sub&gt;CT</td>
<td>48.0/7.4/44.6</td>
<td>7.4</td>
<td>43.9</td>
<td>6.2</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;13&lt;/sub&gt;CT</td>
<td>42.1/13.2/44.7</td>
<td>(6.6)</td>
<td>(42.8)</td>
<td>(7.1)</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;21&lt;/sub&gt;CT</td>
<td>33.9/20.7/45.4</td>
<td>(11.8)</td>
<td>(37.6)</td>
<td>(11.1)</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;29&lt;/sub&gt;CT</td>
<td>26.1/29.1/44.8</td>
<td>(18.8)</td>
<td>(30.8)</td>
<td>(14.0)</td>
</tr>
</tbody>
</table>

| P12PI<sub>7</sub>CT | 46.3/7.0/46.7 | 7.8 | 39.6 | 9.7 | 20.4 | 21.8 | 0.6 | 1.1 | 1.9 | 1.9 | 1.00 |
| P12PI<sub>13</sub>CT | 40.9/12.3/46.8 | (6.5) | (43.2) | (6.5) | (21.8) | (21.4) | (0.5) | (1.1) | (1.9) | (1.9) | (1.00) |
| P12PI<sub>19</sub>CT | 34.8/19.4/45.8 | (9.6) | 39.8 | 8.7 | 20.8 | 20.1 | 1.0 | 1.1 | 1.8 | 1.8 | 0.99 |
| P12PI<sub>25</sub>CT | 29.8/24.9/45.3 | (11.5) | (38.3) | (10.1) | (21.9) | (16.7) | (1.5) | (1.1) | (1.9) | (1.7) | (1.00) |
| P12PI<sub>31</sub>CT | 26.1/29.1/44.8 | (17.8) | (31.9) | (13.5) | (21.0) | (12.1) | (3.8) | (1.2) | (1.9) | (1.5) | (1.00) |
| P12PI<sub>39</sub>CT | 29.8/24.9/45.3 | (23.4) | 27.3 | 14.0 | 20.9 | 9.3 | 5.1 | 1.3 | 1.8 | 1.5 | 1.02 |
| P12PI<sub>40</sub>CT | 22.0/32.6/45.4 | (22.6) | (27.0) | (14.8) | (20.5) | (8.9) | (6.2) | (1.3) | (1.8) | (1.4) | (1.00) |
| P12PI<sub>50</sub>CT | 14.4/39.8/45.8 | 28.2 | 25.0 | 11.4 | 20.2 | 7.5 | 7.8 | 1.4 | 1.8 | 1.4 | 0.99 |
| P12PI<sub>56</sub>CT | 36.4 | 12.5 | 13.8 | 21.4 | 2.6 | 13.4 | 1.5 | 1.9 | 1.2 | 1.02 |

$^a$Experimental values were obtained by the equations mentioned in the text using the $^{13}$C NMR data. Theoretical values (in parentheses) were calculated on the basis of a statistical distribution using the compositional data given in this table.
Table 4-4. Microstructure of P12PIT copolyesters.

<table>
<thead>
<tr>
<th>Copolyesters</th>
<th>Dyads fraction$^a$</th>
<th>Sequence length</th>
<th>Randomness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_{PTP}$</td>
<td>$f_{PTI}$</td>
<td>$f_{ITI}$</td>
</tr>
<tr>
<td>P12PI$_{15}$CT</td>
<td>70.92 (72.42)</td>
<td>26.71 (25.36)</td>
<td>2.38 (2.22)</td>
</tr>
<tr>
<td>P12PI$_{27}$CT</td>
<td>57.51 (53.14)</td>
<td>36.96 (39.51)</td>
<td>5.53 (7.34)</td>
</tr>
<tr>
<td>P12PI$_{41}$CT</td>
<td>33.17 (33.41)</td>
<td>49.49 (47.51)</td>
<td>17.34 (16.89)</td>
</tr>
<tr>
<td>P12PI$_{48}$CT</td>
<td>26.24 (26.97)</td>
<td>51.16 (49.93)</td>
<td>22.60 (23.10)</td>
</tr>
<tr>
<td>P12PI$_{59}$CT</td>
<td>19.08 (16.66)</td>
<td>48.30 (48.31)</td>
<td>32.62 (35.02)</td>
</tr>
<tr>
<td>P12PI$_{66}$CT</td>
<td>11.91 (11.74)</td>
<td>46.18 (45.05)</td>
<td>41.92 (43.21)</td>
</tr>
</tbody>
</table>

$^a$Experimental values were obtained by the equations mentioned in the text using the $^{13}$C NMR data. Theoretical values (in parentheses) were calculated on the basis of a statistical distribution using the compositional data given in the Table 4-2.
\[ R = \left( \frac{1}{L_{PT}} \right) + \left( \frac{1}{L_{IT}} \right) \quad (4 - 7) \]

In these equations, LPT and LIT represent the average length of the 1,2-PD and ISB units, respectively. Table 4-4 provides the theoretical and experimental values of L and R for the P12PIT copolyesters. The theoretical values were calculated for an ideal random copolymer with a Bernoullian distribution using the compositional data from $^1$H NMR analysis. The result indicated that all three copolyesters have essentially random distribution over the entire range of compositions, with values of R being very close to 1, confirming that the structural unit distribution obeys the Bernoullian statistics.\[^{64}\]

**4.3.5. Thermal properties**

Fig. 4-10 shows the second heating scans of all copolyesters, carried out at 10 °C min\(^{-1}\) after the first heating scan and a 5 min isotherm to remove the thermal history. As these scan rates, none of the samples showed the ability to crystallize, so they have the features of a completely amorphous polymer. The PEICT copolyester are already known as
Fig. 4-10. DSC thermograms of PEICT, P12PICT, and P12PIT copolyesters.
amorphous, and 1,2-PD was expected to have lower packing ability compared to EG, so the P12PICT and P12PIT copolyester also could be amorphous.

As shown Table 4-5 and Fig. 4-11, the rigid structure and less flexible nature of ISB dramatically increased $T_g$. The $T_g$ of copolyesters directly increased in proportion to ISB contents from 88 °C to 149 °C. P12PICT copolyesters have slightly higher $T_g$ at similar contents of ISB than PEICT copolyester due to the methyl substituted groups in 1,2-PD, which resulted in the reduced chain flexibility and increased of chain stiffness. In case of P12PIT, it has lower values than PEICT at lower contents of ISB (< 30 mol%) because of the absence of rigid cyclohexane ring of CHDM, however much higher $T_g$ up to about 150 °C could be achieved as an increase of the content of ISB.

To evaluate the thermal stability of the copolyesters, TGA analyses were performed in the 30 °C – 600 °C temperature range under a nitrogen atmosphere. Table 4-5 summarizes the initial degradation temperature at 5 wt% loss of original weight ($T_{5\%}$), the temperature of maximum degradation rate ($T_{\text{max}}$), and the weight percentage of the residue at 600 °C. All copolyesters were thermally stable over 400 °C and
Table 4-5. Thermal properties of PEICT, P12PICT, and P12PIT copolyesters.

<table>
<thead>
<tr>
<th>Copolyesters</th>
<th>DSC&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TGA&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ (°C)</td>
<td>$T_{5%}$ (°C)</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;x&lt;/sub&gt;CT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEI&lt;sub&gt;i&lt;/sub&gt;CT</td>
<td>87.7</td>
<td>410.8</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;i3&lt;/sub&gt;CT</td>
<td>95.6</td>
<td>411.3</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;i21&lt;/sub&gt;CT</td>
<td>103.6</td>
<td>415.1</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;i29&lt;/sub&gt;CT</td>
<td>109.6</td>
<td>409.9</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;x&lt;/sub&gt;CT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i7&lt;/sub&gt;CT</td>
<td>93.9</td>
<td>382.0</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i12&lt;/sub&gt;CT</td>
<td>98.6</td>
<td>381.9</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i19&lt;/sub&gt;CT</td>
<td>102.8</td>
<td>383.3</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i25&lt;/sub&gt;CT</td>
<td>109.8</td>
<td>386.2</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i33&lt;/sub&gt;CT</td>
<td>114.7</td>
<td>392.9</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i40&lt;/sub&gt;CT</td>
<td>121.4</td>
<td>394.9</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;x&lt;/sub&gt;T</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i5&lt;/sub&gt;T</td>
<td>92.6</td>
<td>361.9</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i27&lt;/sub&gt;T</td>
<td>105.6</td>
<td>364.5</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i41&lt;/sub&gt;T</td>
<td>120.3</td>
<td>368.5</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i48&lt;/sub&gt;T</td>
<td>131.5</td>
<td>371.6</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i59&lt;/sub&gt;T</td>
<td>140.9</td>
<td>376.0</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;i66&lt;/sub&gt;T</td>
<td>148.9</td>
<td>379.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> DSC data derived from the second heating run performed at a heating rate of 10 °C min<sup>-1</sup>. $T_g$ = Glass-transition temperature.  
<sup>b</sup> $T_{5\%}$ = Temperature at which a 5% of weight loss occurs, $T_{max}$ = Temperature of the maximum rate of decomposition, RW = Remaining weight at 600 °C.
Fig. 4-11. Glass transition temperature (\(T_g\)) of PEICT (squares), P12PICT (triangles), and P12PIT (diamonds) copolyesters.
displayed rapid decomposition around 400 °C - 450 °C, resulting in less than 3 % - 15 % residual remaining of the initial weight. Unlike the result for \( T_g \), the value of \( T_{5\%} \), \( T_{\text{max}} \), and residue of PEICT was almost same regardless of the contents of diols. In the case of P12PICT, the same trends as PEICT were observed except residue of P12PI\textsubscript{40}CT, but the values are lower than PEICT, probably due to the different bulkiness in structure and lateral methyl group as explained previous section 2.3.4. In case of P12PIT, the values of \( T_{5\%} \) and \( T_{\text{max}} \) become much lower than PEICT or P12PICT, because the more stable CHDM unit was replaced with relatively unstable 1,2-PD and ISB and the molecular weight was lower. But all copolyester has sufficient thermal stability (over 360 °C), and the remaining weight is higher as ISB content increase, potentially due to increased carbonization caused by the presence of the higher oxygen content.

### 4.3.6. Mechanical properties

To evaluate the mechanical properties of copolyesters, tensile assays of each copolyester were carried out using the dumbbell-shaped specimens were prepared by molding as described in the Experimental Section. The mechanical parameters measured in these tests are compared in Table 4-6.
Table 4-6. Mechanical properties of PEICT, P12PICT, and P12PIT copolyesters.

<table>
<thead>
<tr>
<th>Copolyesters</th>
<th>Tensile Properties&lt;sup&gt;a&lt;/sup&gt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Young’s Modulus (MPa)</td>
<td>Yield Strength (MPa)</td>
</tr>
<tr>
<td><strong>PEI&lt;sub&gt;1&lt;/sub&gt;CT</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEI&lt;sub&gt;1&lt;/sub&gt;CT</td>
<td>1,360 ± 73</td>
<td>42.9 ± 0.5</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;13&lt;/sub&gt;CT</td>
<td>1,370 ± 7</td>
<td>43.1 ± 0.1</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;21&lt;/sub&gt;CT</td>
<td>1,430 ± 60</td>
<td>44.9 ± 0.2</td>
</tr>
<tr>
<td>PEI&lt;sub&gt;26&lt;/sub&gt;CT</td>
<td>1,480 ± 67</td>
<td>45.2 ± 0.3</td>
</tr>
<tr>
<td><strong>P12PI&lt;sub&gt;1&lt;/sub&gt;CT</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;1&lt;/sub&gt;CT</td>
<td>1,440 ± 35</td>
<td>44.2 ± 0.1</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;12&lt;/sub&gt;CT</td>
<td>1,420 ± 27</td>
<td>44.8 ± 0.1</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;19&lt;/sub&gt;CT</td>
<td>1,470 ± 11</td>
<td>46.0 ± 0.1</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;25&lt;/sub&gt;CT</td>
<td>1,440 ± 12</td>
<td>46.3 ± 0.1</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;33&lt;/sub&gt;CT</td>
<td>1,590 ± 40</td>
<td>48.1 ± 0.5</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;40&lt;/sub&gt;CT</td>
<td>1,550 ± 50</td>
<td>49.0 ± 1.0</td>
</tr>
<tr>
<td><strong>P12PI&lt;sub&gt;1&lt;/sub&gt;T</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;41&lt;/sub&gt;T</td>
<td>1,550 ± 18</td>
<td>49.9 ± 2.4</td>
</tr>
<tr>
<td>P12PI&lt;sub&gt;48&lt;/sub&gt;T</td>
<td>1,720 ± 54</td>
<td>57.2 ± 0.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> Obtained from the tensile test at RT, averaged from tests performed at 5 mm min<sup>-1</sup> for PEI<sub>x</sub>CT and P12PI<sub>x</sub>CT or 1 mm min<sup>-1</sup> for P12PI<sub>x</sub>T with injection molded samples of 2 mm X 2 mm X 10 mm.
In case of P12PIT except for P12PI_{41}T and P12PI_{48}T, preparation of
dumbbell-shaped specimens or measurement was limited due to brittleness.

Compared PEICT and P12PICT at the similar content of ISB, the
yield strength of P12PIT was higher than PEICT; this can be explained by
the existence of lateral methyl group as seen from the result of P12PCT
compare to PECT in the previous chapter 2. Although there was no
statistical difference in Young’s modulus (P >0.05) as shown in Fig. 4-12,
the trend that values of P12PICT were little higher than the modulus of
PEICT at the same ISB content. On the one hand, there was no statistical
difference between P12PI_{40}CT and P12PI_{41}T, and the others could not be
compared because the range of ISB contents was different.

When evaluating the influence of ISB in each copolyester series,
both Young’s modulus and the yield strength increase as increase of ISB
content for all copolyesters, and the differences became much bigger in
case of P12PIT series. These results come from that rigidity between
monomers was significantly different in P12PICT due to the absence of
CHDM. Recently, Park et al.\textsuperscript{[113]} synthesized ISB based polycarbonate
with CHDM, the T\textsubscript{g}, storage, and Young’s modulus, and tensile strength of
copolycarbonates was increased as the ratio of ISB increases. However, the
ISB content greater than 50 mol% made the copolycarbonates strong but brittle, these results are good agreement with data in this experiment.

**Fig. 4-12.** Young’s modulus and yield strength of PEICT, P12PICT, and P12PIT copolyesters.
4.4. Conclusion

By introducing ISB as a comonomer into the P12PCT copolyesters, new P12PICT terpolyesters with high $T_g$ were synthesized, and the microstructure and properties were compared to PEICT copolyesters. Compare to PEICT, P12PICT had higher ISB contents and $T_g$ at same ISB feed ratio, even if compared to PEICT with same ISB content, P12PICT displayed higher $T_g$ due to the lateral methyl group. Furthermore, P12PIT copolyesters excluding CHDM were also successfully obtained. In case of P12PIT, the reactivity ratio of ISB became higher than P12PICT; the residual ratio of ISB increased up to over 55 $\%$, and the $T_g$ of P12PIT copolyesters were noticeably high up to about 150 $^\circ$C. These novel copolyesters have adequate molecular weights and nearly random sequence. All the copolyesters were amorphous and showed sufficient thermal stability (over 360 $^\circ$C). The rigidity of ISB monomer made the copolyester stiffer and brittle and produced higher yield strength and Young’s modulus.
Chapter 5.

Conclusions
Five kinds of new partially biobased copolyesters, P12PCT, P23BCT, P13BCT, P12PICT, and P12PIT, were synthesized using three potentially biobased diols, 1,2-PD, 2,3-BD, and 1,3-BD, which have a high potential as biobased chemicals, but the limited literature on monomer of polyester.

In the first part, polymerization of 1,2-PD or 2,3-BD with CHDM and DMT yielded two new polyester series, P12PCT, and P23BCT, which have the same skeletal structure as PETG. Although the increase of the ethylene diol in the feed made it hard to obtain high molecular weight copolymers due to the low reactivity of the secondary hydroxyl group, P12PCT and P23BCT copolyesters displayed lower densities, higher T\text{g}, and stiffer mechanical properties compared with PECT with a similar ethylene diol content. This could be explained the lateral methyl group of ethylene diol reduced chain flexibility, that is, produced an effect on enhancing the potential barriers to the rotation and the influence led to the increase of chain stiffness and T\text{g}. This trend that the substituted methyl group made the polymer chain stiffer was also supported by theoretical calculations of group contribution approach. The most notable effect resulting from the lateral methyl group was the notable increase in T\text{g}, the T\text{g} of P23B_{48}CT (94.5 °C) and P23B_{65}CT (95.6 °C) were extremely higher than that of PE_{53}CT.
(80.9 °C) and PE_{69}CT (71.9 °C) despite its lower molecular weight.

In chapter 3, the catalyst played a key role in the synthesis of P13BCT, the results of polymerization of two catalysts were significantly different depending on side reaction. The mechanism of side reaction was clarified by analyzing the side-product using GC-MS. In case of tin catalyst, the dehydration reaction of 1,3-BD was occur and the major product, 3-butene-1-ol, made a vinyl end group stopping the growth of polymer chain. On the other hand, titanium catalyst made it possible to obtain the P13BCT copolyesters with high molecular weight although with increasing 1,3-BD content, the molecular weight became lower because of the lower reactivity of the secondary hydroxyl group. As increasing the contents of the 1,3-BD units, the density and yield strength slightly increased, whereas thermal stability, $T_g$, and crystallinities decreased.

Lastly, by introducing isosorbide (ISB) into the P12PCT copolyesters, new P12PICT terpolyesters with high $T_g$ were synthesized, and P12PIT copolyesters excluding CHDM were also successfully obtained, the copolyesters with higher biobased content and higher $T_g$ could be obtained. Compare to PEICT, P12PICT had higher ISB contents and $T_g$ at same ISB feed ratio, even if compared to PEICT with same ISB content, P12PIT
displayed higher T$_g$ due to the lateral methyl group. In case of P12PIT, the reactivity ratios of ISB increased by became higher than those of P12PICT or PEICT; the copolyester had more biobased contents and higher T$_g$ up to 150 °C. These novel copolyesters have adequate molecular weights and nearly random sequence. The rigidity of ISB monomer made the copolyester stiffer and brittle and produced higher yield strength and Young’s modulus.
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Supporting Information

S1. Calculation of Glass Transition Temperatures ($T_g$) of PET, P12PT, P23BT, and PCT

As shown below (eq. S1), the glass transition temperature ($T_g$) can be predicted from *Molar Glass Transition Function* ($Y_g$), which is product $T_g \cdot M$ and behaves in general as additive function approved by Van Krevelen and Hoftyzer (1975).[66]

$$T_g = \frac{Y_g}{M} = \sum \frac{Y_{gi}}{M}$$  \hspace{1cm} \text{(eq. S1)}

The $T_g$ of each polyester can be calculated from group contribution parameters in Table S1-1 considering each repeating unit structure as shown in the Table S1-2. The $T_g$ increase in the order PET, P12PT, PCT, P23BT and these trends prove that the effect to increase $T_g$ raise in the order EG, 1,2-PD, CHDM, 2,3-BD, which are is in complete agreement with the slope in Fig. 2-8.
### Table S1-1. Group contributions to $Y_g$ (K kg mol$^{-1}$)

<table>
<thead>
<tr>
<th>Group</th>
<th>$Y_g$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_2$-</td>
<td>2.7</td>
</tr>
<tr>
<td>-CH(CH$_3$)-</td>
<td>8.0</td>
</tr>
<tr>
<td><img src="image.png" alt="Diagram" /></td>
<td>62</td>
</tr>
<tr>
<td><img src="image.png" alt="Diagram" /></td>
<td>25$^b$</td>
</tr>
</tbody>
</table>

$^a Y_g$ = Molar glass transition function, which is expected from Table 6.1 and Table 6.3 in Ref. [66]. $^b$ The value is calculated considering the ratio of cis/trans (25/75).

### Table S1-2. Calculation parameters and $T_g$ of PET, P12PT, P23BT, and PCT.

<table>
<thead>
<tr>
<th>Polyesters</th>
<th>$Y_g$ $^a$</th>
<th>$M$ $^b$</th>
<th>$T_g$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>67.4</td>
<td>192.1</td>
<td>350.9</td>
</tr>
<tr>
<td>P12PT</td>
<td>72.7</td>
<td>206.1</td>
<td>352.7</td>
</tr>
<tr>
<td>P23BT</td>
<td>78.0</td>
<td>220.1</td>
<td>354.4</td>
</tr>
<tr>
<td>PCT</td>
<td>87</td>
<td>246.2</td>
<td>353.4</td>
</tr>
</tbody>
</table>

$^a Y_g$ = Molar glass transition function, which is calculated from Table S1-1 by additive group contribution method. $^b M$ = Molar mass of repeating unit. $^c T_g$ = glass transition temperature, which is calculated using (eq. S1).
S2. Prediction of Young’s Modulus (E) of PET, P12PT, and P23BT

There are theoretical inter-relations between elastic parameters, bulk modulus (K), shear modulus (G) and tensile modulus (E) as shown in the (eq. S2).[66] The bulk modulus and shear modulus can be calculated from Molar Elastic Wave Function, U; it is independent of temperature or polymeric phase state and can be calculated from additive group contribution as can be seen from (eq. S3) - (eq. S4). So the tensile modulus or Young’s modulus (E) can be estimated from (eq. S2) - (eq. S5).

\[
E = \frac{3G}{(1 + \frac{1}{3}(G/K))} \quad (\text{eq. S2})
\]

\[
K = \rho \left(\frac{U_R}{V}\right)^6 \quad (\text{eq. S3})
\]

\[
G = \rho \left(\frac{U_H}{V}\right)^6 \quad (\text{eq. S4})
\]

\[
G/K = \left(\frac{U_H}{U_R}\right)^6 \quad (\text{eq. S5})
\]

The Young’s modulus of each polyester was calculated from group contribution parameters in Table S2-1 considering each repeating unit structure. As shown in the Table S2-2, the modulus increase in the order PET, P12PT, P23BT and these trends supported that the substituted methyl group made the polymer chain stiffer.
Table S2-1. Group contributions to the Rao and Hartmann-functions.

<table>
<thead>
<tr>
<th>Group</th>
<th>(U_R^a)</th>
<th>(U_H^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\text{CH}_2)-</td>
<td>880</td>
<td>675</td>
</tr>
<tr>
<td>(-\text{CH(CH}_3)-</td>
<td>1,875</td>
<td>1,650</td>
</tr>
<tr>
<td></td>
<td>1,225</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>4,100</td>
<td>3,300</td>
</tr>
</tbody>
</table>

\(^a\) \(U_R =\) Rao-function, \(U_H =\) Hartmann function, \((\text{cm}^3/\text{mol})(\text{cm/s})^{1/3}\) which are expected from Table 14.4 in Ref. [66].

Table S2-2. Calculation parameters and Young’s modulus of PET, P12PT, and P23BT.

<table>
<thead>
<tr>
<th>Polyesters</th>
<th>(\rho^a)</th>
<th>(V^b)</th>
<th>(U_R^c)</th>
<th>(U_H^c)</th>
<th>(G/K^d)</th>
<th>(G^d)</th>
<th>(E^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>1.33</td>
<td>144.4</td>
<td>8,310</td>
<td>6,450</td>
<td>0.22</td>
<td>2.73E+09</td>
<td>5,330</td>
</tr>
<tr>
<td>P12PT</td>
<td>1.25</td>
<td>164.9</td>
<td>9,305</td>
<td>7,425</td>
<td>0.26</td>
<td>2.73E+09</td>
<td>7,550</td>
</tr>
<tr>
<td>P23BT</td>
<td>1.21</td>
<td>181.9</td>
<td>10,300</td>
<td>8,400</td>
<td>0.29</td>
<td>3.74E+09</td>
<td>10,200</td>
</tr>
</tbody>
</table>

\(^a\) \(\rho = \) Density, which is obtained from the linear trend line equations of Fig. 2-1. The density is y-axis intercept in the graph. \(^b\) \(V = \) Molar volume of repeating unit, which is the values, molar mass \((M)\) divided by density \((\rho)\). \(^c\) \(U_R =\) Rao-function, \(U_H =\) Hartmann function, which is calculated from Table S2-1 by additive group contribution method. \(^d\) \(G/K =\) ratio of shear modulus to bulk modulus, \(G =\) shear modulus, \(E =\) Tensile or Young’s modulus, which is estimated using (eq. S5), (eq. S4), and (eq. S2), respectively.
S3. Synthesis results of P12PIT with DBTO catalyst

The different results of polymerization between DBTO and TBT catalyst are compared in Table S3-1. As similar to P13BCT case (refer to section 3.3.1), the resulting polyesters using DBTO attained smaller molecular weight than one of using TBT catalyst, especially as the 1,2-PD content is higher. However, the difference of molecular weight and vinyl end group contents between catalysts were very small compared to P13BCT. This could be for the following reasons that the side reaction including dehydration of 1,2-propanediol is hard to occur, whereas 1,3-propanediol or 1,3-butanediol easily dehydrate to 2-propen-1-ol or 3-butene-1-ol.\textsuperscript{91}

Fig. S3-1 displays the representative $^1$H NMR spectra of P13BCT and P13BCT_Sn copolyester with peak assignment confirming the existence of vinyl end group resulting from side reaction.
Table S3-1. Composition and characteristics of the synthesized P12PIT copolyesters.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Code</th>
<th>Feed ratio&lt;sup&gt;a&lt;/sup&gt; 1,2-PD/ISB</th>
<th>Composition ratio&lt;sup&gt;b&lt;/sup&gt; 1,2-PD/ISB</th>
<th>Molecular weight&lt;sup&gt;cd&lt;/sup&gt;</th>
<th>IV&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$M_n$</td>
<td>$M_w$</td>
</tr>
<tr>
<td>1</td>
<td>P12PI&lt;sub&gt;15&lt;/sub&gt;T</td>
<td>180/20</td>
<td>85.1/14.9</td>
<td>9 000</td>
<td>23 200</td>
</tr>
<tr>
<td>2</td>
<td>P12PI&lt;sub&gt;27&lt;/sub&gt;T</td>
<td>160/40</td>
<td>72.2/26.8</td>
<td>10 700</td>
<td>27 800</td>
</tr>
<tr>
<td>3</td>
<td>P12PI&lt;sub&gt;41&lt;/sub&gt;T</td>
<td>140/60</td>
<td>57.8/41.2</td>
<td>14 600</td>
<td>38 000</td>
</tr>
<tr>
<td>4</td>
<td>P12PI&lt;sub&gt;48&lt;/sub&gt;T</td>
<td>120/80</td>
<td>51.9/48.1</td>
<td>11 700</td>
<td>37 000</td>
</tr>
<tr>
<td>5</td>
<td>P12PI&lt;sub&gt;55&lt;/sub&gt;T</td>
<td>100/100</td>
<td>40.8/59.2</td>
<td>14 800</td>
<td>33 200</td>
</tr>
<tr>
<td>6</td>
<td>P12PI&lt;sub&gt;66&lt;/sub&gt;T</td>
<td>80/120</td>
<td>34.3/65.7</td>
<td>15 600</td>
<td>35 000</td>
</tr>
<tr>
<td>7</td>
<td>P12PI&lt;sub&gt;41&lt;/sub&gt;T_Sn</td>
<td>140/60</td>
<td>58.6/4.2&lt;sup&gt;c&lt;/sup&gt;/41.2</td>
<td>6 000</td>
<td>13 700</td>
</tr>
<tr>
<td>8</td>
<td>P12PI&lt;sub&gt;37&lt;/sub&gt;T_Sn</td>
<td>140/60</td>
<td>60.2/2.9&lt;sup&gt;c&lt;/sup&gt;/38.6</td>
<td>8 600</td>
<td>22 500</td>
</tr>
<tr>
<td>9</td>
<td>P12PI&lt;sub&gt;46&lt;/sub&gt;T_Sn</td>
<td>120/80</td>
<td>51.5/2.2&lt;sup&gt;c&lt;/sup&gt;/46.3</td>
<td>12 000</td>
<td>62 800</td>
</tr>
<tr>
<td>10</td>
<td>P12PI&lt;sub&gt;58&lt;/sub&gt;T_Sn</td>
<td>100/100</td>
<td>40.8/1.4&lt;sup&gt;c&lt;/sup&gt;/57.8</td>
<td>14 100</td>
<td>34 000</td>
</tr>
<tr>
<td>11</td>
<td>P12PI&lt;sub&gt;67&lt;/sub&gt;T_Sn</td>
<td>80/120</td>
<td>32.0/1.0&lt;sup&gt;c&lt;/sup&gt;/67.0</td>
<td>13 200</td>
<td>29 700</td>
</tr>
</tbody>
</table>

<sup>a</sup> Molar ratio in the initial feed. The excess of a diol concerning DMT was in all cases achieved with 1,3-BD.  
<sup>b</sup> Molar composition determined by integration of the $^1$H-NMR spectra.  
<sup>c</sup> Molar ratio of vinyl end group.  
<sup>d</sup> $M_n$: number average molecular weight in g mol$^{-1}$, $M_w$: weight average molecular weight in g mol$^{-1}$, PDI: polydispersity index.  
<sup>e</sup> Intrinsic viscosity in dL g$^{-1}$ measured in o-chlorophenol at 30 °C.
Fig. S3-1. $^1$H-NMR spectra of copolyesters of (a) P12PL$_{41}$T$_{Sn}$ and (b) P12PL$_{41}$T copolyesters.
국문 요약

적용 사례가 드물었던 1,2-프로판디올과 2,3-부탄디올, 1,3-부탄디올을 에틸렌 디올대신 기존 고분자에 적용하여 새로운 폴리에스터를 합성하였다. 또한 1,2-프로판디올과 아이소소바이드를 활용하여 유리전이 온도가 향상된 새로운 폴리에스터를 중합하였다. 각 시리즈별로 모노머의 함량 조성을 다양하게 조절하여 모노머의 종류 및 함량에 따른 고분자의 중합도 및 물성에 대한 영향을 살펴 보았다. 한편 측량별로 반응성이 달라지는 경우 부산물 분석을 통해 부반응의 경로 및 중합도가 올라가지 않는 이유를 밝혀내었다. 카본 핵자기 공명 분광법을 이용하여 고분자 사슬의 시퀀스 분석을 수행하였고, 이를 통해 모노머의 반응성 및 고분자의 자유도를 알아볼 수 있었다. 그 외 열분석 및 결정성, 사출을 통한 인장물성 평가 등을 통해 고분자 물성을 평가하였다.

첫번째로 기존의 에틸렌 글리콜의 고분자 (PECT, PETG로도 불림)와 같은 동격을 갖는 새로운 코폴리에스터 (P12PCT, P23BCT)를 합성하였을 때에는 메틸 치환기의 수 및 함량에 따라 고분자의 중합도 및 물성이 달라짐을 알 수 있었다. 메틸렌 사이드 그룹에
의해 부피가 늘어나 밀도가 낮아지고, 또한 고분자 사슬의 유동성이 낮아지면서 유리전이 온도가 높아지고, 인장강도 및 모듈러스가 상대적으로 높아졌다. 특히 2,3-부탄디올을 이용한 코폴리에스터 (P23BCT)의 경우에는 기존의 에틸렌글리콜을 이용한 고분자 (PECT)보다 유리전이온도가 15도 가까이 매우 크게 향상되었다. 반면 메틸 치환기로 인해 열분해반응이 쉽게 일어나 열안정성은 약간 떨어졌다.

두번째로는 1,3-부탄디올을 적용하여 중합을 하였는데, 이전과 같은 주석계열의 촉매를 사용한 경우에는 탈수반응이 일어나 부탄디올이 아닌 한쪽 끝이 에틸렌 부산울이 생성되어 말단기로 남겨되어 중합도가 올라가지 않을을 부산물의 가스크로마토그래피-질량 분석 및 핵자기공명 분석을 통해 알아내었다. 촉매를 티탄계열로 교환하여 고분자의 새로운 폴리에스터를 얻을 수 있었으며, 밀도와 인장강도는 증가하였으나, 유리전이 온도 및 열안정성은 떨어짐을 알 수 있었다.

마지막으로 아이소소바이드를 도입하여 1,2-프로판디올과 중합함으로서 기존의 상업화된 코폴리에스터 (PEICT)보다 유리전이
온도가 높은 새로운 코폴리에스터(P12PICT)를 합성하였으며 여기서 1,4-사이들로 핵산디메탄올 모노머를 제외하여 보다 바이오매스의 함량과 유리전이 온도가 높은 새로운 폴리에스터(P12PIT)를 증합하였다. 아이소소바이드 함량이 가장 높은 P12PI66T의 경우 유리전이 온도가 150도까지 상승하였다. 탄소 핵자기 공명 분광법을 이용하여 조성에 상관없이 모든 폴리에스터가 베르누이 분포를 따르면서 자유도가 1에 가까음을 확인하였다.

주요어: 재생가능 자원, 바이오베이스 폴리에스터, 2,3-부탄디올, 1,2-프로판디올, 아이소소바이드, 1,3-부탄디올, 1,4-사이들로 핵산디메탄올, 고분자 중합

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