# Novel Potentially Biobased Copolyesters Comprising 1,3-Butanediol, 1,4-Cyclohexanedimethanol and Dimethyl Terephthalate; Effect of Different Catalysts on Polymerization Behavior

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**Abstract:** A new series of potentially biobased copolyesters, poly(1,3-butylene 1,4-cyclohexylenedimethylene terephthalate) (P13BCT) based on 1,3-butanediol (1,3-BD) with 1,4-cyclohexane dimethanol (CHDM) was synthesized. Dibutyltin oxide (DBTO) and titanium(IV) butoxide (TBT) catalysts were employed, and the resulting copolymers were analyzed to evaluate the efficacy of each catalyst on the copolymerization. DBTO produced low molecular weight oligomers with $M_n$ ranging from 2,000 to 2,500, whereas TBT produced high molecular weight copolymer $M_n$ ranging from 8,700~21,900. GC-MS analysis was performed to identify the by-products during the transesterification process, and side reactions such as dehydration were observed, which were in good agreement with previous results showing the same by-product. The correlation spectroscopy (COSY), heteronuclear single-quantum correlation spectroscopy (HSQC), ^{1}H and ^{13}C NMR analyses revealed that the chain end of P13BCT_Sn was primarily composed of the vinyl end group rather than the hydroxyl group, which was a major contributor to the formation of low molecular weight polymers. The density of P13BCT slightly increased with the addition of 1,3-BD. The $T_g$ of P13BCT decreased with 1,3-BD contents from 74 ℃ to 51 ℃ due to the enhanced flexibility of the main chain. The thermal stability of the copolyesters was determined using TGA in a nitrogen atmosphere. The copolyesters were stable up to 330-360 ℃, and the decomposition temperature decreased as the 1,3-BD content increased. Yield strength increased from 39.4 MPa to 43.6 MPa as 1,3-BD content increased; however, Young's modulus and yield strength difference was not statistically significant.
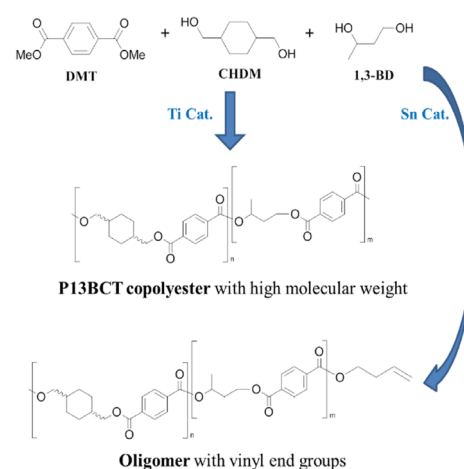
**Keywords:** copolyesters, potentially biobased, catalysts, polycondensation.

## 1. Introduction

Biobased polymers have attracted considerable attention in the last decades, considering the increased concerns on the scarcity of fossil fuels and global warming.[1-3] Among the various types of polymers, the development of biobased polyesters highlights novel methods of synthesizing biobased polymers because bio-resourced monomers are readily accessible, and resulting polymers exhibit a unique and wide range of properties such as mechanical properties and biodegradability, leading to diverse applications in the field of packaging and engineering plastics.[4]

Butanediol (BD) possesses four stable structural isomers;

1,2-, 1,3-, 1,4-, and 2,3-butanediol. Biobased 1,4-BD is commercially produced by a number of companies and is used industrially as a solvent as well as in the manufacture of plastics and elastic fibers, specifically, poly(butylene terephthalate) (PBT) and poly(butylene succinate) (PBS). 2,3-BD is a precursor of many chemical products, including solvents such as methyl ethyl ketone, gamma-butyrolactone, and 1,3-butadiene.[5] Since the 1910s, researchers have been studying microbial productions of 2,3-BD; many studies have improved strains, alternative fermentation substrates, improved cultivation techniques, downstream processing, and derivative production.[6] The low reactivity of 2,3-BD's secondary hydroxyl groups makes it difficult to produce high molecular weight polyesters.[7-9] Several attempts have been reported to synthesize high molecular weight polyester with 2,3-BD as a comonomer.[10,11] Although 1,3-BD is an important chemical used in the production of polymers, antibiotics, pheromones, and insecticides,[12] a bioprocess for mass production of 1,3-BD using a renewable raw material and natural, synthetic pathway has not yet been developed.[13] 1,3-BD has been produced via multistep chemical reactions starting with acetaldehyde, and several researchers have recently constructed 1,3-BD pro-

duction routes using various microbial strains.[14-16] Although 1,3-BD can be used as a polyester monomer, it is difficult to find related studies to produce polyesters using 1,3-BD compared to reports of polyester synthesis using 1,4-BD or 2,3-BD. Only low molecular weight copolymers of 1,3-BD and adipic acid were developed as a plasticizer for polyvinylchloride or polylactic acid.[17-19]

Our previous study synthesized new copolyesters with 1,4-cyclohexanedimethanol (CHDM) and dimethyl terephthalate (DMT) using 2,3-BD instead of ethylene glycol.[20] The two primary hydroxyl groups of CHDM are attributed to the increased reactivity for the copolymerization in comparison to the comonomers with secondary hydroxyl groups showing poor reactivity. Biobased CHDM is produced in two consecutive hydrogenation steps and comprises 70% trans and 30% cis isomers. It is also reported that the cyclohexane ring in CHDM exists in either the chair or boat conformation. The ring flips between the two conformations increase chain mobility, leading to the improved mechanical properties of copolymers.[21-22]

In polyester synthesis, the catalyst plays an important role in obtaining high molecular weight polyesters. Despite its importance, the catalyst mechanism in the polycondensation reaction is poorly understood because severe reaction conditions, such as high temperature and high vacuum, do not allow quantitative and qualitative analyses of the polycondensation process.[23] Current research is primarily focused on the antimony, germanium, and titanium catalyst series for commercial production of poly(ethylene terephthalate) (PET).[24] Recently, several studies on the catalyst for the polymerization of copolyesters, exist;[10,25-28] however, most results were limited to a simple screening test and did not explain in detail the cause of the different polymerization results depending on the type of catalyst used.

In this study, copolymerization of 1,3-BD with CHDM and DMT produced a new copolyester series, poly(1,3-butylene 1,4-cyclohexylene-dimethylene terephthalate) (P13BCT). Notably, the choice of catalyst, either dibutyltin oxide (DBTO) or titanium (IV) butoxide (TBT), resulted in a difference in polymerization degree and side reaction occurrence. The detailed analysis of products and by-products led to the investigation of the role and the mechanism of catalysts on the copolymerization reactions.

## 2. Experimental

### 2.1. Materials

DMT (99.9%), CHDM (99.8%) with 70 mol % of the *trans* isomer, 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.

### 2.2. Synthesis of the copolyesters

P13BCT copolyesters were synthesized by melt polymerization in two steps, transesterification and polycondensation. 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. The reaction

mixture was heated from 180 to 220 ℃ 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 intervals for analysis. For the polycondensation reaction, the temperature was gradually increased to 235 ℃, 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 then quenched product was dried in a vacuum oven for 15 h at 60 ℃.

### 2.2.1. P13B$_x$CT copolyesters

$^1$H NMR (600 MHz; CDCl$_3$, $\delta$): 8.11 (4H, Ar$\underline{H}$), 5.41 (1H, OC$\underline{H}$CH$_3$), 4.71 (2H, OC$\underline{H_2}$CH$_2$), 4.31 (4H, OC$\underline{H_2}$CH (*cis*)), 4.20 (4H, OC$\underline{H_2}$CH (*trans*)), 2.27 (2H, OCH$_2$C$\underline{H_2}$), 2.0~1.1 (10H, cyclohexane ring), 1.46 (3H, OCHC$\underline{H_3}$). $^{13}$C NMR (150 MHz; CDCl$_3$, $\delta$): 166.0-165.3 (C=O), 134.3-133.9 (ArC), 130.1-129.7 (ArC), 70.3 (O$\underline{C}$H$_2$CH (*trans*)), 69.4 (O$\underline{C}$HCH$_3$), 68.2 (O$\underline{C}$H$_2$CH (*cis*)), 62.0 (O$\underline{C}$H$_2$CH$_2$), 34.8 (OCH$_2$$\underline{C}$H$_2$), 37~25 (cyclohexane ring), 20.4 (CH$\underline{C}$H$_3$).

### 2.2.2. P13B$_x$CT_Sn copolyester with DBTO catalyst

$^1$H NMR (600 MHz; CDCl$_3$, $\delta$): 8.11 (4H, Ar$\underline{H}$), 5.8(1H, CH$_2$=C$\underline{H}$CH$_2$), 5.41 (1H, OC$\underline{H}$CH$_3$), 5.2~5.1 (2H, C$\underline{H_2}$=CHCH$_2$), 4.5 (2H, OC$\underline{H_2}$CH$_2$), 4.4 (2H, CHCH$_2$C$\underline{H_2}$O), 4.31 (4H, OC$\underline{H_2}$CH (*cis*)), 4.20 (4H, OC$\underline{H_2}$CH (*trans*)), 2.6 (2H, CH$_2$=CHC$\underline{H_2}$), 2.3 (2H, OCH$_2$C$\underline{H_2}$), 2.0~1.1 (10H, cyclohexane ring), 1.46 (3H, OCHC$\underline{H_3}$). $^{13}$C NMR (150 MHz; CDCl$_3$, $\delta$): 166.0-165.3 (C=O), 134.3-134.0 (ArC), 130.4(CH$_2$=$\underline{C}$HCH$_2$), 129.7 (ArC), 117.7 ($\underline{C}$H$_2$=CHCH$_2$), 70.3 (O$\underline{C}$H$_2$CH (*trans*)), 69.4 (O$\underline{C}$HCH$_3$), 68.2 (O$\underline{C}$H$_2$CH (*cis*)), 64.6 (CHCH$_2$$\underline{C}$H$_2$O), 62.0 (O$\underline{C}$H$_2$CH$_2$), 34.8 (OCH$_2$$\underline{C}$H$_2$), 33.3 (CH$_2$=CH$\underline{C}$H$_2$), 37~25 (cyclohexane ring), 20.4 (CH$\underline{C}$H$_3$).

### 2.3. Characterization

The intrinsic viscosity of the polyesters was measured using an automated Ubbelohde viscometer (SKYVIS) at a concentration of 0.2 g dL$^{-1}$ in *o*-chlorophenol at 30 ℃. The number and weight average of molecular weight, as well as molecular weight distribution, were determined by GPC using *o*-chlorophenol: chloroform (1:3, v/v) as a mobile phase at a velocity of 0.7 mL min$^{-1}$ equipped with two Shodex LF804 columns at 40 ℃. Molecular weights were estimated against monodisperse polystyrene standards. Densities of the copolyesters were measured by Archimedes' principle using an AND GR 200 balance equipped with an AD-1653 density determination kit.

$^1$H and $^{13}$C NMR spectra were obtained using a JEOL ECA-600 spectrometer operating at 600 and 150 MHz, respectively, with deuterated chloroform (CDCl$_3$) as a solvent. Tetramethylsilane (TMS) was used as an internal standard and as a reference for the chemical shifts. The by-products were analyzed by gas chromatography-mass spectrometry (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. Pyridine solutions containing 5 vol.% of the samples were injected into the injection port set at 250 ℃ with a split ratio of 30:1. The column was

heated at 50 ℃ to 250 ℃ at a rate of 5 ℃/min and held for 5 min. The identification of all compounds was achieved using the NIST11 mass spectral data library. The quantification was done by the area normalization method.

Differential scanning calorimetry (DSC) analysis was performed on a Mettler-Toledo DSC 820 calorimeter. Pellet samples of about 10 mg were enclosed in standard 40 μL aluminum cells. The samples were melted at 300 ℃ for 5 min and then quenched to 30 ℃ at a rate of 300 ℃ min⁻¹. The temperature was then increased at a rate of 10 ℃ min⁻¹ from 30 to 300 ℃, under a nitrogen atmosphere. The glass transition temperature ($T_g$) was estimated 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 exothermic and endothermic peaks appearing on the heating trace, respectively. Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA 7 with vertical balance instruments from 30 ℃ to 600 ℃ at a scan rate of 10 ℃ min⁻¹ under a nitrogen gas atmosphere.

## 3. Results and discussion

### 3.1. Synthesis and reaction mechanism of P13BCT copolyesters

A two-step growth polycondensation reactions of DMT, CHDM, and potentially biobased 1,3-BD were used to synthesize the copolyesters. The reaction path is shown in Scheme 1. The copolyesters are designated as P13B$_x$CT, where the subscripts x denotes the molar content of 1,3-BD units in the copolymer. As shown in Table 1, copolyesters with 1,3-BD and CHDM at molar ratios ranging from 115/85 to 170/30 were prepared using a DMT feed molar ratio to total diols of 1:2, with an excess of 1,3-BD, which has a lower boiling point than CHDM. The temperature was maintained at 180 ℃ for 3 h to prevent volatilization of the 1,3-BD, then increased to 220 ℃ to prevent oligomer crystallization. To remove the volatile by-products, the polycondensation reaction was performed under vacuum for 2 h at 235 ℃. Table 1 compares the copolymerization results for various diols molar ratios and the differences between DBTO and TBT catalysts. Although DBTO was previously known to be an
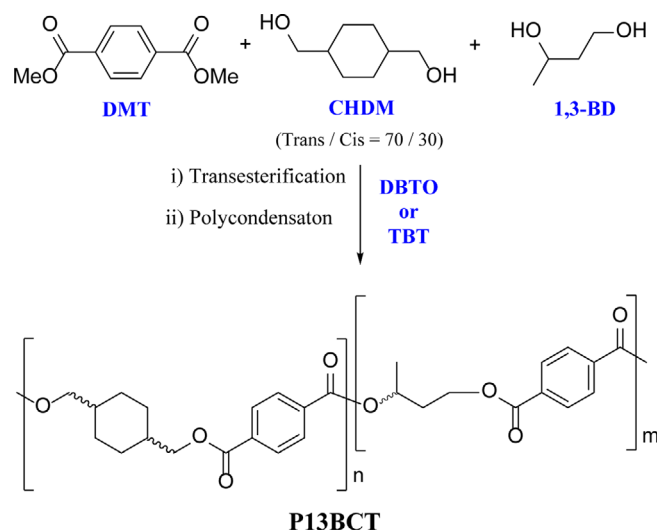


**Scheme 1.** Polymerization reaction leading to P13BCT.

efficient catalyst to produce high molecular weight polymers,[10,29] the resulting polyesters using DBTO had extremely low molecular weight oligomers, with intrinsic viscosities of .ca 0.1 dL g⁻¹ and number-average molecular weight ($M_n$) ranging from 2,000 to 2,500 g mol⁻¹. On the other hand, replacing DBTO with TBT catalyst resulted in P13BCT with intrinsic viscosities above 0.4 dL g⁻¹ and $M_n$ around 8,700~21,900.

GC-MS analysis was conducted to identify the by-products collected by temperature during the transesterification reaction. As shown in Figure 1, in the case of the DBTO catalyst, several unexpected by-products were detected on GC-MS, except for methanol, and their identifications are listed in Table 2. The amount of side reactions increased as the reaction temperature was gradually increased from 180 ℃ to 220 ℃. A probable reaction pathway from 1,3-BD to by-products is shown in Scheme 2. Previous studies have reported a similar reaction mechanism for 1,3-BD dehydration and oxidation in the vapor phase over solid acids such as SiO₂-Al₂O₃, CeO₂-ZrO₂, and TiO₂ catalysts.[30,31] Although the catalysts and reaction conditions were not the same in this study as in previous reports, the transesterification reaction temperature of over 200 ℃ appeared to be high enough to initiate these side reactions. More importantly,

**Table 1.** Composition and characteristics of the synthesized P13B$_x$CT copolyesters

| Entry | Code | Feed ratio[a] CHDM/1,3-BD | Composition ratio[b] CHDM/1,3-BD | Molecular weight[d] | | | IV[e] |
|---|---|---|---|---|---|---|---|
| | | | | $M_n$ | $M_w$ | PDI | |
| | | | Tin (DBTO) catalyst | | | | |
| 1 | P13B$_{21}$CT_Sn | 70/130 | 70.4/21.3/8.2[c] | 1,050 | 3,000 | 2.86 | 0.11 |
| 2 | P13B$_{37}$CT_Sn | 50/150 | 50.4/36.5/13.1[c] | 1,020 | 2,130 | 2.09 | 0.11 |
| 3 | P13B$_{57}$CT_Sn | 30/170 | 32.7/57.2/10.1[c] | 1,000 | 2,400 | 2.41 | 0.10 |
| | | | Titanium (TBT) catalyst | | | | |
| 4 | P13B$_{29}$CT | 85/115 | 71.4/28.6 | 21,900 | 60,500 | 2.76 | 0.68 |
| 5 | P13B$_{38}$CT | 70/130 | 62.0/38.0 | 17,300 | 49,400 | 2.86 | 0.56 |
| 6 | P13B$_{52}$CT | 50/150 | 48.4/51.6 | 11,200 | 41,400 | 3.69 | 0.48 |
| 7 | P13B$_{69}$CT | 30/170 | 30.8/69.2 | 8,700 | 32,300 | 3.71 | 0.39 |

[a]Molar ratio in the initial feed. The excess of a diol concerning DMT was in all cases achieved with 1,3-BD. [b]Molar composition determined by integration of the ¹H NMR spectra. [c]Molar ratio of vinyl end group. [d]$M_n$: number average molecular weight in g mol⁻¹, $M_w$: weight average molecular weight in mol⁻¹, PDI: polydispersity index. [e]Intrinsic viscosity in dL g⁻¹ measured in o-chlorophenol at 30 ℃.
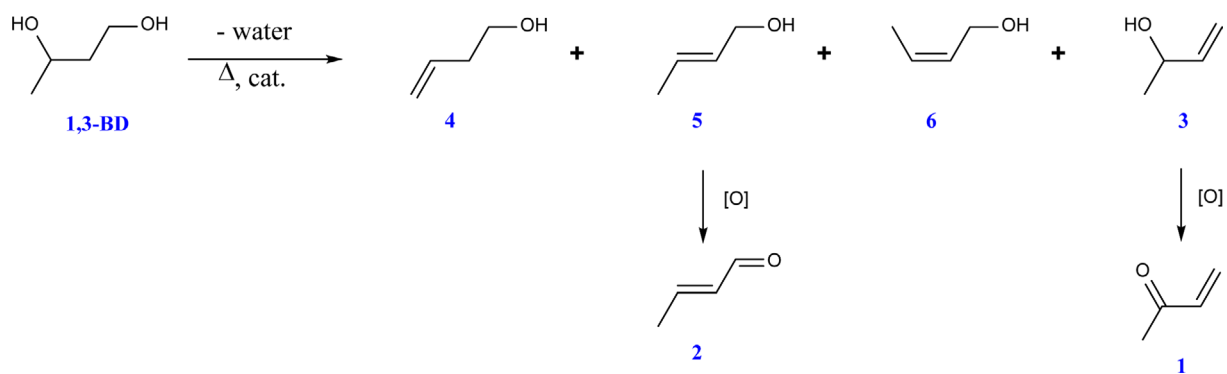
**Scheme 2.** Probable reaction pathway from 1,3-BD to by-products over the tin catalyst.



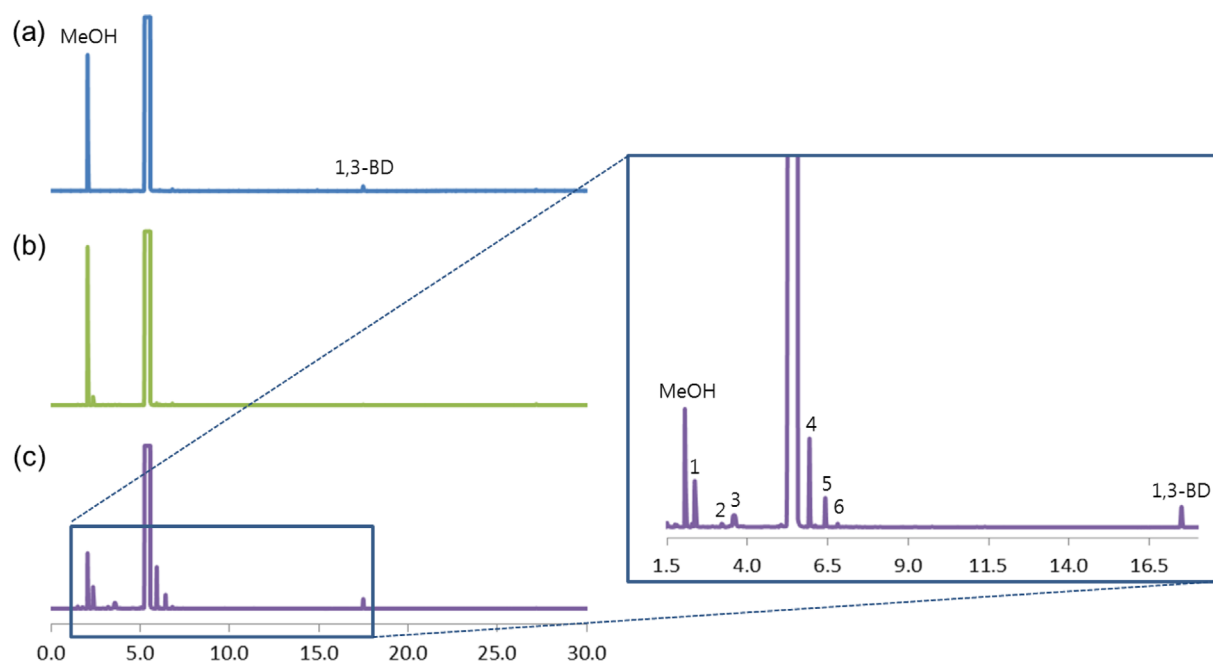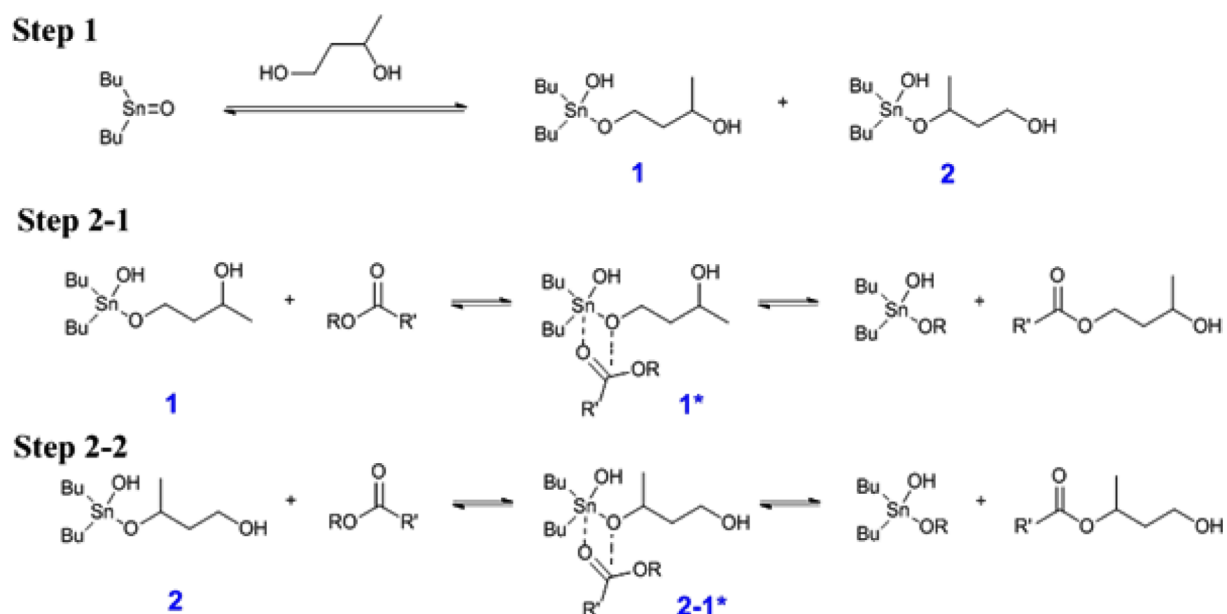**Figure 1.** GC-MS chromatograms of MeOH and other by-product solution during transesterification reaction of P13BCT_Sn (a) at 180 ℃ for an initial 2 h. (b) at 200 ℃ following 2 h. (c) at 220 ℃ for the last 1 h.



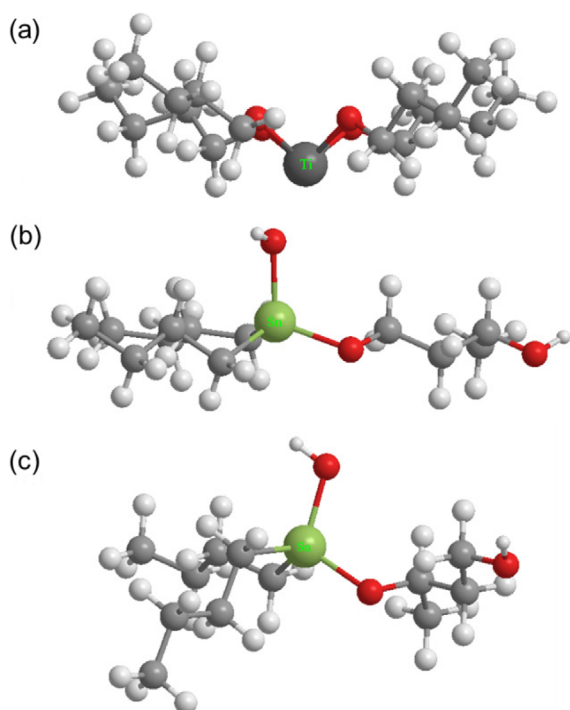**Scheme 3.** Mechanism of transesterification reaction with DBTO catalyst and 1,3-BD.

**Figure 2.** Optimized geometries of (a) the TBT catalyst, (b) the tin alkoxide 1, and (c) the tin alkoxide 2 in Scheme 3.

dration reaction of various diols with the CeO$_2$ catalyst. In these studies, 1,3-diols such as 1,3-propanediol (1,3-PD) and 1,3-BD were selectively dehydrated to allylic alcohol, whereas 1,2-propanediol (1,2-PD) and 2,3-BD were barely dehydrated. These results also explained why copolyesters containing 1,2-PD or 2,3-BD polymerized successfully with DBTO in our previous study.[20]

On the one hand, a TBT catalyst composed entirely of alkoxide is expected to be less active and acidic than a DBTO catalyst. The mechanism for catalyzed transesterification processes by dialkyl tin derivatives[34] or titanium alkoxides[35] is known, and it is a coordinative pathway involving the formation of a complex between a carbonyl group and the metal atom. Following the formation of tin alkoxides by the reaction of DBTO with alcohols (step 1), there was transferred complexation of the carboxylic acid with the tin alkoxide by the insertion of the carboxylic group (step 2-1 or 2-2), as shown in Scheme 3. Otherwise, because TBT was already in its oxide form, it could directly coordinate with the carbonyl group without going via the step 1 reaction. Based on the hydroxyl group, there are two possible structures of tin alkoxide (1 and 2 in Scheme 3), and the suggested structures of these catalysts are compared in Figure 2. The tin alkoxide 2 was expected to exist at low concentrations because of the low reactivity of the secondary hydroxyl group, and the transesterification was difficult to achieve due to steric hindrance, as shown in Figure 2(c). According to these hypotheses, step 2-1 was the most important for polycondensation, and the end groups of polymer chains would be primarily composed of the secondary hydroxyl group of 1,3-BD.
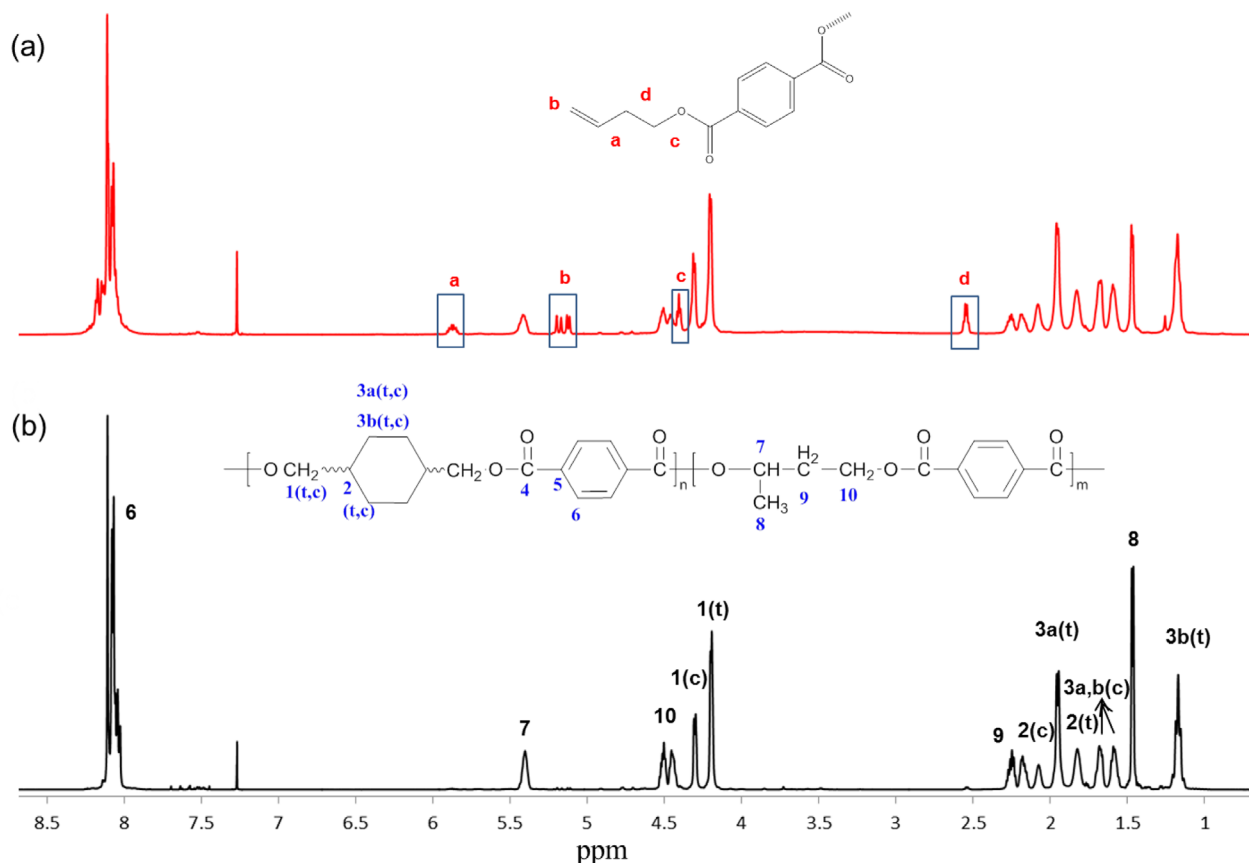
except for methanol, the highest peak, as shown in Figure 1, was 3-butene-1-ol, which was in good agreement with the previous results.[20] There are other reports[32,33] concerning the dehy-



**Figure 3.** $^1$H NMR spectra of copolyesters of (a) P13B$_{37}$CT_Sn and (b) P13B$_{52}$CT copolyesters.
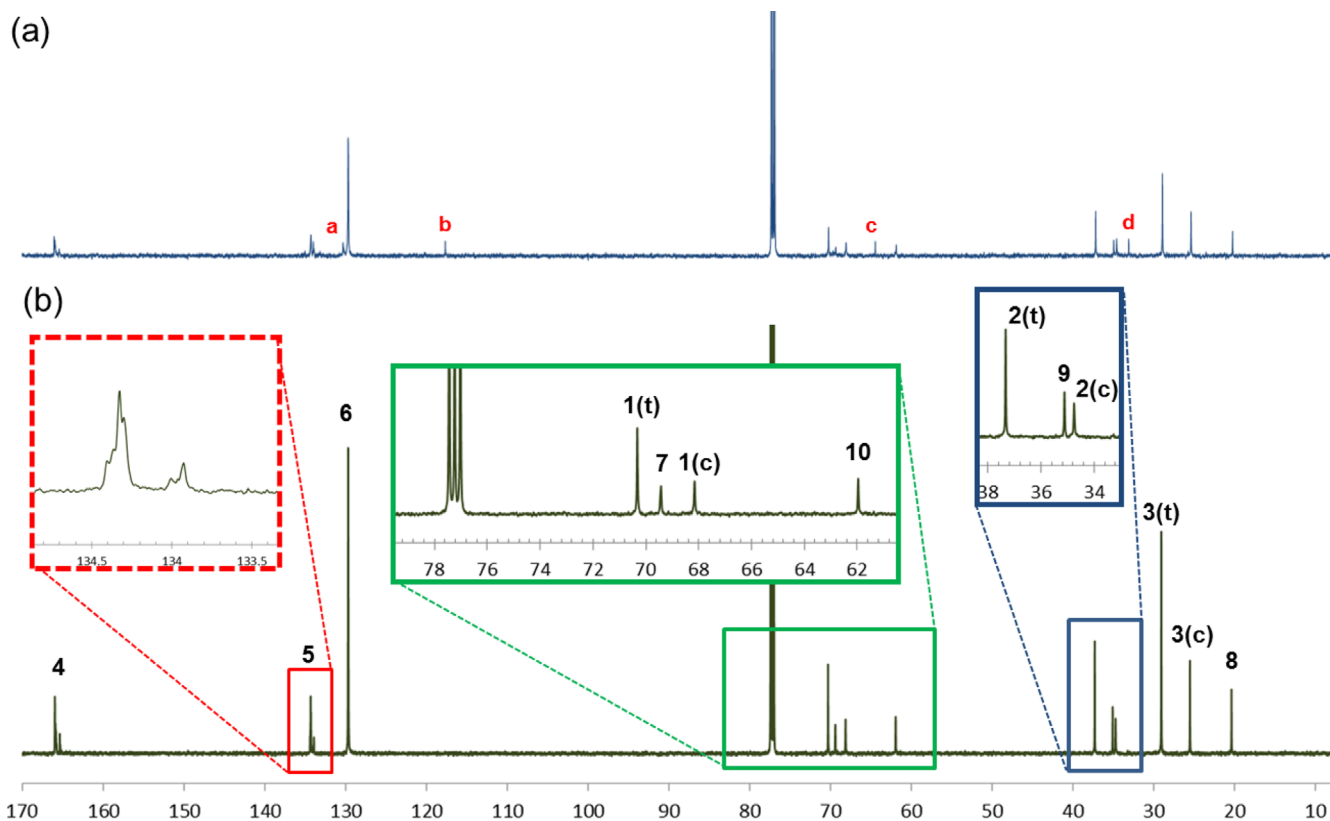
**Figure 4.** $^{13}$C NMR spectra of copolyesters of (a) P13B$_{37}$_Sn and (b) P13B$_{52}$CT.
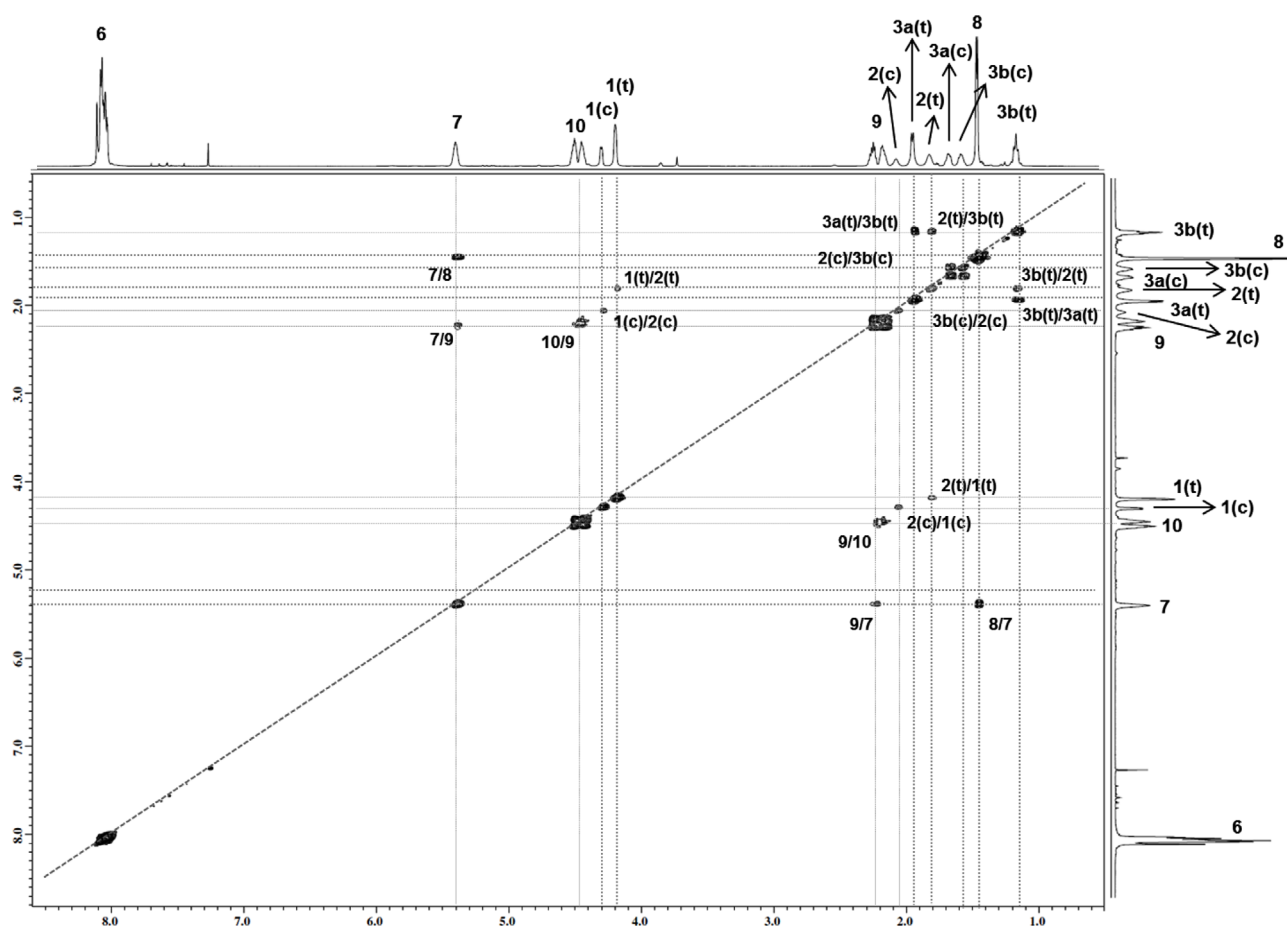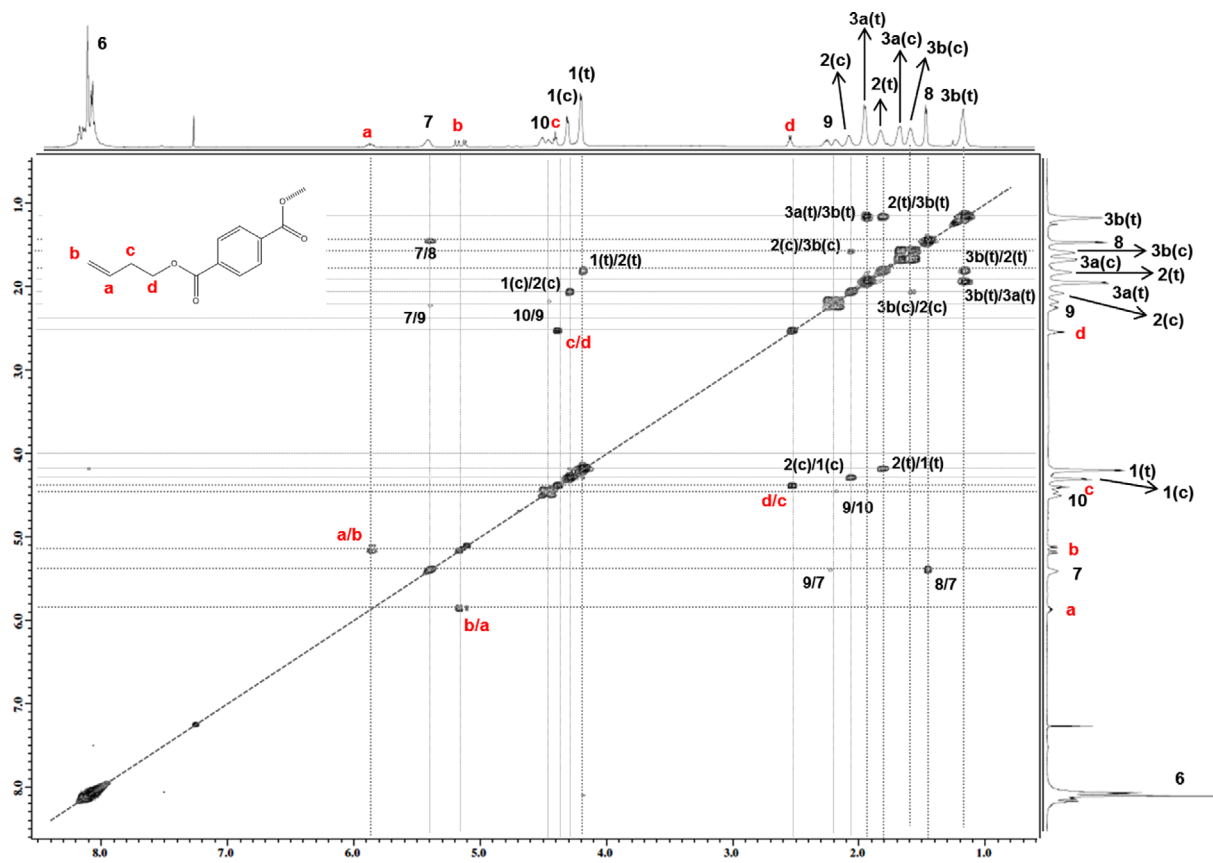


**Figure 5.** Correlation (COSY) spectra of P13B$_{52}$CT.

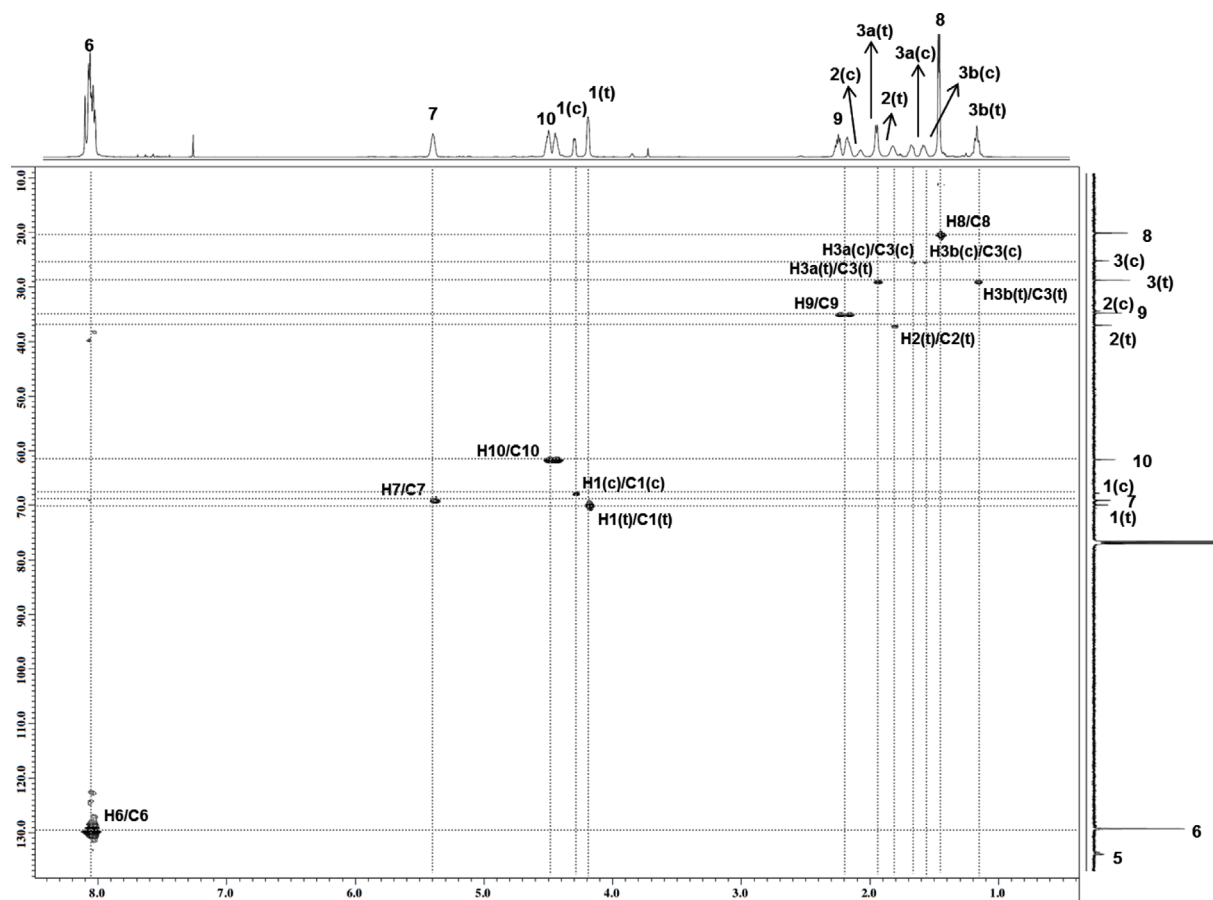**Figure 6.** Correlation (COSY) spectra of P13B$_{37}$CT_Sn.



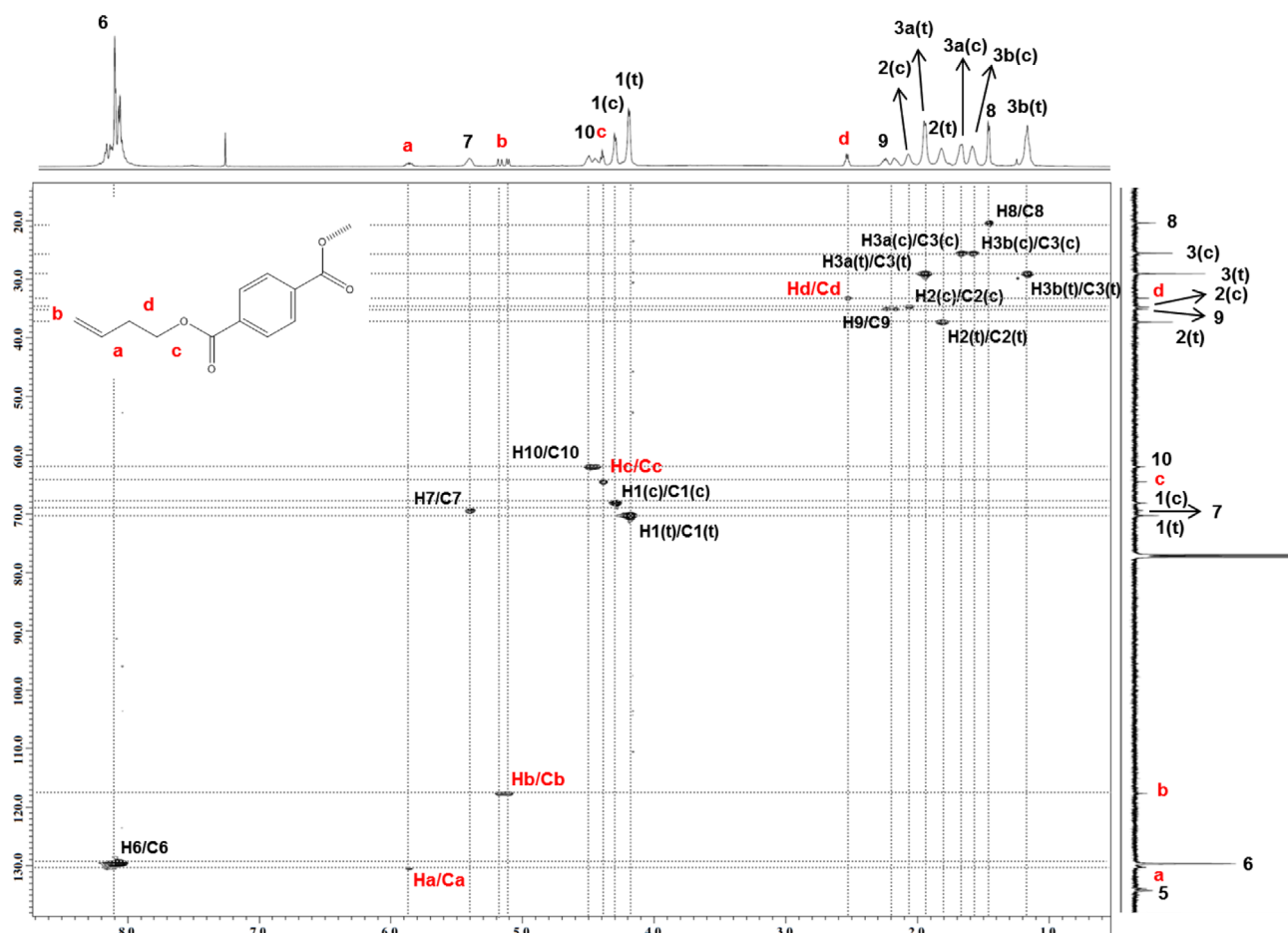**Figure 7.** Heteronuclear single-quantum correlation (HSQC) spectra of P13B$_{52}$CT.

**Figure 8.** Heteronuclear single-quantum correlation (HSQC) spectra of P13B$_{37}$CT_Sn.

## 3.2. Structure analysis

1D and 2D NMR spectroscopy were used to analyze the chemical structure and composition of P13BCT copolyesters. Detailed NMR assignments are listed in the experimental section. Representative $^1$H and $^{13}$C NMR spectra of P13BCT are shown in Figures 3 and 4, along with peak assignments. In the case of a P13BCT with a tin catalyst, several unknown peaks originating from side-products were observed. Using 2D NMR spectra and NMR simulation software, the side-product signals were identified as the vinyl end group generated by 3-butene-1-ol. Figures 5 and 6 show the correlation spectroscopy (COSY) spectra of P13r3B$_{69}$CT and P13B$_{37}$CT_Sn, respectively. The heteronuclear single-quantum correlation spectroscopy (HSQC) spectra of P13B$_{69}$CT and P13B$_{37}$CT_Sn are shown in Figures 7 and 8.

The copolyester compositions were determined by quantifying the proton signals in $^1$H NMR spectra. The peaks of the 1,3-BD moiety in the P13BCT at $\delta$ 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 $\delta$ 4.31, 4.20, and 2.0-1.1 ppm were assigned to hydrogen atoms 1(*cis*), 1(*trans*), and a cyclohexane ring. The vinyl group peaks at $\delta$ 5.8, 5.2-5.1, and 2.6 ppm in the P13BCT with the tin catalyst were assigned to hydrogen atoms a, b, c, d, respectively. The composition was determined by quantifying the proton signals emitted by the oxymethylene (7) of the 1,3-BD, the oxymethylene (1) of CHDM (sum of *trans* and *cis*), and

the vinyl hydrogen (a). Except for P13B$_{29}$CT and P13B$_{38}$CT, CHDM remained nearly constant with feed ratio, assuming that all excess 1,3-BD was removed during the polycondensation reaction (Table 1). The vinyl end group content of P13BCT with the tin catalyst was extremely high (8-13 mol%), which was a major contributor to the formation of low molecular weight polymers.

Pham *et al*. used $^1$H and $^{13}$C NMR to analyze the end group of poly(1,3-butylene adipate), Reoplex®. Reoplex® has a similar molecular weight ($M_n$ = 1,950, $M_w$ = 4,000) to P13B$_x$CT_Sn in this study, and the chain-ends were composed of 28.6% primary alcohol and 71.4% of a secondary alcohol, with peaks located at 1.7-1.8 ppm and 3.5-5.3 ppm regions of $^1$H resonances.[18] However, no peaks were observed in the same regions in the case of P13BCT_Sn, demonstrating that the P13BCT_Sn chain

**Table 2.** List of by-products during transesterification of P13B$_{37}$CT_Sn detected by GC-MS

| No | GC/MS | | |
|----|-------|----------|-------|
| | RT$^a$ (min) | Compound | MW$^b$ |
| 1 | 1.55 | 3-Buten-2-one | 70 |
| 2 | 2.13 | 2-Butenal | 70 |
| 3 | 2.44 | 3-Buten-2-ol | 72 |
| 4 | 3.64 | 3-Buten-1-ol | 72 |
| 5 | 4.39 | 2-Buten-1-ol | 72 |
| 6 | 4.38 | 2-Buten-1-ol, (Z) | 72 |

$^a$RT: retention time. $^b$MW: molecular weight (g mol$^{-1}$).

**Table 3.** Densities and Thermal properties of P13B$_x$CT copolyesters

| Copolyesters | Density[a] | DSC[b] | | | | | TGA[c] | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $T_g$ (℃) | $T_c$ (℃) | $\Delta H_c$ (J/g) | $T_m$ (℃) | $\Delta H_m$ (J/g) | $T_{5\%}$ (℃) | $T_{max}$ (℃) | RW (%) |
| P13B$_{29}$CT | 1.19 | 74.1 | 145.4 | 25.1 | 235.8 | 26.6 | 360.5 | 375.2 | 5.4 |
| P13B$_{38}$CT | 1.20 | 68.2 | 155.1 | 17.7 | 212.8 | 18.3 | 350.4 | 412.8 | 7.2 |
| P13B$_{52}$CT | 1.21 | 59.8 | - | - | - | - | 339.0 | 401.1 | 7.5 |
| P13B$_{69}$CT | 1.22 | 50.6 | - | - | - | - | 332.3 | 362.3 | 6.1 |

[a]Density in g mL$^{-1}$. [b]DSC data derived from the second heating run performed at a heating rate of 10 ℃ min$^{-1}$. $T_g$ = Glass-transition temperature, $T_c$ = crystallization temperature, $\Delta H$ = enthalpy of transition, $T_m$ = melting temperature. [c]$T_{5\%}$ = Temperature at which a 5% of weight loss occurs, $T_{max}$ = Temperature of the maximum rate of decomposition, RW = Remaining weight at 600 ℃.

end was primarily composed of the vinyl end group rather than the hydroxyl group.

The microstructures of the copolyesters were determined using $^{13}$C NMR and two non-protonated aromatic carbons, which are more sensitive to the sequence than any other carbon atoms due to through-space and through-bond interactions between neighboring monomers.[36] As shown in the dotted red box in Figure 4, non-protonated aromatic carbons with chemical shifts around 134 ppm did not split enough to distinguish the dyad microstructure.

### 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, and the density of P13BCT slightly increased with the content of 1,3-BD, which is completely consistent with the volumes relationship between CHDM and 1,3-BD.

DSC was used to analyze the thermal transition behavior of the copolyesters, and the detailed data, $T_g$, $T_c$, $T_m$, and corresponding enthalpies ($\Delta H_c$, and $\Delta H_m$), are listed in Table 3. The $T_g$ of P13BCT copolyesters steadily decreased as 1,3-BD contents increased from 74 ℃ to 51 ℃ due to increased chain flexibility. A crystallization peak and melting peak were found in the case of P13B$_{29}$CT and P13B$_{38}$CT with lower 1,3-BD diol content, and the peaks became smaller with higher 1,3-BD contents.

TGA was used to evaluate the thermal stability of the copolyesters in a nitrogen atmosphere. Table 3 shows the initial degradation temperature at 5 wt% loss of original weight ($T_{5\%}$), the maximum degradation rate temperature ($T_{max}$), and the weight percentage of the residue at 600 ℃. All copolyesters demonstrated sufficient thermal stability; they were stable up to 330-360 ℃ and decomposed rapidly between 360-410 ℃. Additionally, the residual weight left after heating at 600 ℃ was about 5-8% of the initial weight. The decomposition temperature decreased as the 1,3-BD content increased, possibly due to the lateral methyl group and lower molecular weight of 1,3-BD.

### 3.4. Mechanical properties

Tensile testing on an injection-molded specimen was used to evaluate the mechanical properties of the P13BCT copolyesters. The measured mechanical parameters are summarized in Table 4. In the case of P13B$_{69}$CT, preparation of dumbbell-shaped specimens was limited due to the poor mechanical properties, which

**Table 4.** Mechanical properties of P13BxCT copolyesters

| Copolyesters | Tensile properties[a] | | |
|---|---|---|---|
| | Yong's modulus (MPa) | Yield strength (MPa) | Elongation at break (%) |
| P13B$_{29}$CT | 1190 ± 17 | 39.4 ± 0.2 | 174 ± 8 |
| P13B$_{38}$CT | 1220 ± 62 | 42.3 ± 0.1 | 104 ± 14 |
| P13B$_{52}$CT | 1220 ± 41 | 43.6 ± 0.1 | 54 ± 10 |

[a]Obtained from the tensile test at RT, averaged from tests performed at 5 mm/min with injection molded samples of 2 mm × 2 mm × 10 mm.

resulted from its low molecular weights. The polymeric chains stiffened as the 1,3-BD contents increased, leading to the enhanced yield strength from 39.4 MPa to 43.6 MPa. Young's modulus increased slightly around 1,200 MPa, but the increase was not significant, probably due to the low molecular weights of polymers and the increase in the 1,3-BD contents in the polymeric chains. The values of elongation at break showed the same dependence on the molecular weights. In addition to the effect of molecular weight on Young's modulus ($P > 0.05$), yield strength decreased with cyclohexylene content; this can be explained by the conformational transition of the cyclohexylene ring, the motions of which were found to be associated with the secondary relaxation of these copolymers.[37,38]

### 4. Conclusions

New potentially biobased copolyesters, poly(1,3-butylene 1,4-cyclohexylenedimethylene terephthalate) series, were synthesized by 1,3-BD and CHDM using DBTO and TBT as catalysts. According to GC-MS and NMR analyses, 3-butene-1-ol was a significant by-product, with the remaining vinyl end groups at the chain end limiting polymer chain growth. In the case of the TBT catalyst, P13BCT copolyesters with high molecular weight were obtained. With increasing 1,3-BD content, high molecular weight polymers became more difficult to obtain because of the lower reactivity of the secondary hydroxyl group. The density and yield strength slightly increased as the 1,3-BD content increased, whereas thermal stability, $T_g$, and crystallinities decreased as the number of aliphatic carbons increased.

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