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# A Zn-MOF-Catalyzed Terpolymerization of Propylene Oxide, $CO_2$, and β-butyrolactone

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Received: 22 August 2018; Accepted: 11 September 2018; Published: 13 September 2018


**Abstract:** The terpolymerization of propylene oxide (PO), $CO_2$, and a lactone is one of the prominent sustainable procedures for synthesizing thermoplastic materials at an industrial scale. Herein, the one-pot terpolymerization of PO, $CO_2$, and β-butyrolactone (BBL) was achieved for the first time using a heterogeneous nano-sized catalyst: zinc glutarate (ZnGA-20). The reactivity of both PO and BBL increased with the $CO_2$ pressure, and the polyester content of the terpolymer poly (carbonate-co-ester) could be tuned by controlling the infeed ratio of PO to BBL. When the polyester content increased, the thermal stability of the polymers increased, whereas the glass transition temperature ($T_g$) decreased.

**Keywords:** heterogeneous catalysis; metal-organic frameworks; zinc glutarate; terpolymerization; $CO_2$; β-butyrolactone; biodegradable polymers; poly(alkylene carbonates); poly(hydroxybutyrates)

## 1. Introduction

The conversion of $CO_2$ into chemical commodities, particularly the synthesis of biodegradable poly(alkylene carbonates) by the alternating copolymerization of an epoxide and $CO_2$, is regarded as one of the most sustainable approaches for the use of $CO_2$ as a source material in large-scale industrial processes [1–11]. Poly(alkylene carbonates) are characterized by a variety of properties, e.g., lightness, strength, durability, high transparency, heat resistance, and good electrical insulating ability. They are applied as adhesives, coating and packing materials, and binders in ceramic industries. Furthermore, they are important candidates for biomedical applications because of their low toxicity, biocompatibility, and biodegradability [1,7,12,13].

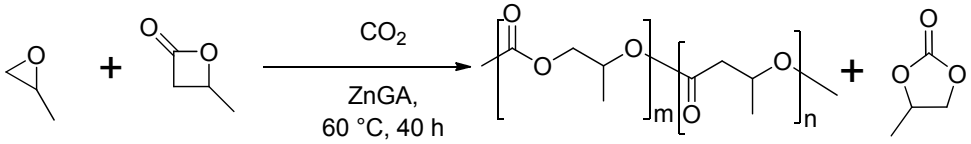
The copolymerization of epoxides and $CO_2$ was first reported by Tsuruta and Inoue [2,3] in 1969, since when a variety of homogeneous and heterogeneous catalysts have been developed for the copolymerization of $CO_2$ and epoxides [7,14–25]. Among these catalysts, zinc glutarate (ZnGA) has been widely employed as a heterogeneous catalyst in industry because it is economical and nontoxic, can be easily synthesized and dealt with, and affords high-molecular-weight copolymers [7,11,21,24,25].

In particular, ZnGA catalyzes the copolymerization of propylene oxide (PO) and $CO_2$ to afford poly(propylene carbonate) (PPC) with high molecular weight and a glass transition temperature ($T_g$) of ~40 °C [7]. However, the thermal stability and biodegradability of PPC still remain to be enhanced for a wide range of industrial applications [7,13]. In this context, to modify the thermal and mechanical properties of the PPCs, the terpolymerization of PO and $CO_2$ with a third monomer has been presented as an economic and environmentally benign method [26–28]. To this end, ZnGA has been used as a catalyst in the terpolymerization of PO and $CO_2$ with several monomers, including lactones, cyclic anhydrides, and other epoxides [29–40].

Among them, lactones are interesting candidates because their ring opening polymerization affords the poly(hydroxyalkanoates) (PHA), a burgeoning class of thermoplastic polymers with enhanced biodegradability and thermal properties [41]. These PHA are useful in packaging films, drug release and biomedical implants [41–44]. Among these, the most common polyesters are the poly(3-hydroxy butyrates) (PHB), which are well known for their biocompatibility and biodegradability [45–48]. PHB can be inexpensively prepared by the ring opening polymerization of β-butyrolactone (BBL) [49–55].

Therefore, from an industrial point of view, including PHB segments in PPC would provide an opportunity to positively tune the mechanical and thermal properties and to enhance their biodegradability, thereby widening the applicability range of the both PHB and PPC. Here, using BBL as the third monomer in the ZnGA catalyzed copolymerization of PO and $CO_2$ could be envisaged as being a prolific method that would allow to insert PHB segments randomly in PPC. However, it was not until 2017 that the terpolymerization of an epoxide, $CO_2$, and BBL was realized; indeed, BBL, despite its high ring strain, appears to be a less reactive monomer than higher lactones [45]. More recently, Rieger et al. [56] reported the homogeneous zinc-catalyzed one-pot synthesis of AB, ABA block terpolymers from BBL, cyclohexene oxide (CHO), and $CO_2$, where the selectivity could be tuned by $CO_2$.

From this background, the terpolymerization of PO, BBL, and $CO_2$ still remains to be achieved. Herein, as part of our continued research efforts to improve the catalytic activity of ZnGA and explore additional applications for ZnGA [11], we report the ZnGA-catalyzed terpolymerization of PO, BBL, and $CO_2$ (Scheme 1), which affords poly(ester-co-carbonates) with thermal and mechanical properties that can be tuned by adjusting the ratio of PO to BBL in the feedstock.




**Scheme 1.** Terpolymerization of PO, BBL, and $CO_2$ using ZnGA-20.

## 2. Results and Discussion

### *2.1. Synthesis and Characterization of Nano-Sized ZnGA*

Nano-sized ZnGA (ZnGA-20) was prepared according to previous reports with slight modifications [6]. Briefly, glutaric acid (1.321 g, 10.0 mmol) was stirred in anhydrous toluene (20.0 mL) under a nitrogen atmosphere. Then, ZnO (0.814 g, 10.0 mmol) was introduced and the suspension was stirred at 20 °C for 24 h. The resulting white precipitates were then filtered and thoroughly washed with an excess of acetone before drying at 130 °C under vacuum for 12 h. The particles were then analyzed using powder X-ray diffraction (PXRD) and Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) isotherm analysis. The PXRD pattern of the as-prepared ZnGA-20 and the pattern calculated from the crystal structure are compared in Figure 1a, which clearly shows all the typical reflexes for ZnGA, implying that ZnGA-20 and standard ZnGA share the same crystal lattice. Among all the reflexes, three strong reflexes at 2θ values of ~12.5°, ~22.5°, and ~23.0° were selected, and their Miller indices were found to be (200), (210), and (20−2), respectively. The coherence length ($Lc_{(hkl)}$), which is a measure of crystal quality, was calculated from the full width at half maximum (FWHM) values of the corresponding reflexes using Scherer's equation, and the results are summarized in Table S1. The overall crystallinity (Xc) of the catalyst was calculated to be 69.1% from the deconvoluted crystalline and amorphous regions of the PXRD pattern (Table S1).

The corresponding FT-IR spectroscopic analysis shows the typical bands for ZnGA (Figure 1b) [6]. Thus, the $COO^-$ antisymmetric stretching bands were observed at ~1584 $cm^{-1}$ and ~1405 $cm^{-1}$,

a $COO^-$ symmetric stretching band was observed at 1538 $cm^{-1}$, and the CH stretching and $CH_2$ scissoring bands appeared at 2955 $cm^{-1}$ and 1445 $cm^{-1}$, respectively. Figure 1c displays a SEM image of ZnGA-20, which exhibits nano-sized rectangular platelets with approximately 80 nm × 70 nm of length and width, respectively, and an average thickness lower than 20 nm. Moreover, the BET isotherm analysis of ZnGA-20 shows that the catalyst is a mesoporous material with a mean pore size of 32.4 nm and a surface area of 22.7 $m^2/g$, being these values typical of ZnGA frameworks (Table S1).

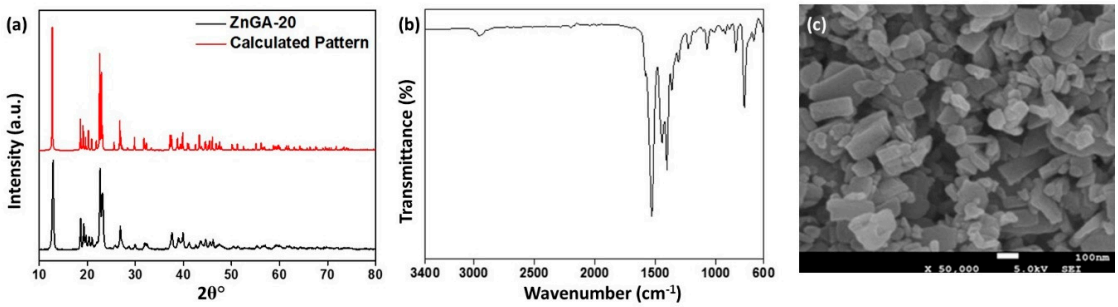



**Figure 1.** (**a**) PXRD pattern of ZnGA-20 and PXRD pattern calculated from the crystal structure of ZnGA via Mercury 3.7 [57], (**b**) FT-IR spectrum, and (**c**) SEM image of ZnGA-20.

### *2.2. Terpolymerization of PO, BBL, and $CO_2$ using ZnGA-20 as the Catalyst*

With catalyst ZnGA-20 in hand, we set out to investigate its catalytic activity in the terpolymerization of PO, $CO_2$, and BBL under different reaction conditions. Initially, the terpolymerization was attempted with 30 equivalents of a 1:1 mixture of PO and BBL and 1 equivalent of ZnGA-20 at 60 °C in the presence of 1.5 MPa of $CO_2$ for 40 h. The resulting reaction mixture was analyzed using $^1$H-NMR spectroscopy (Figure 2) to find that the formation of the expected terpolymer had occurred and was accompanied by a small amount of cyclic propylene carbonate (PC). It should be noted, here, that although some other metal organic framework (MOF) systems were reported to produce cyclic carbonates as a product in the reaction of $CO_2$ with an epoxide, the ZnGA is the only MOF to produce poly(alkylene carbonate) as a major product [58–61].

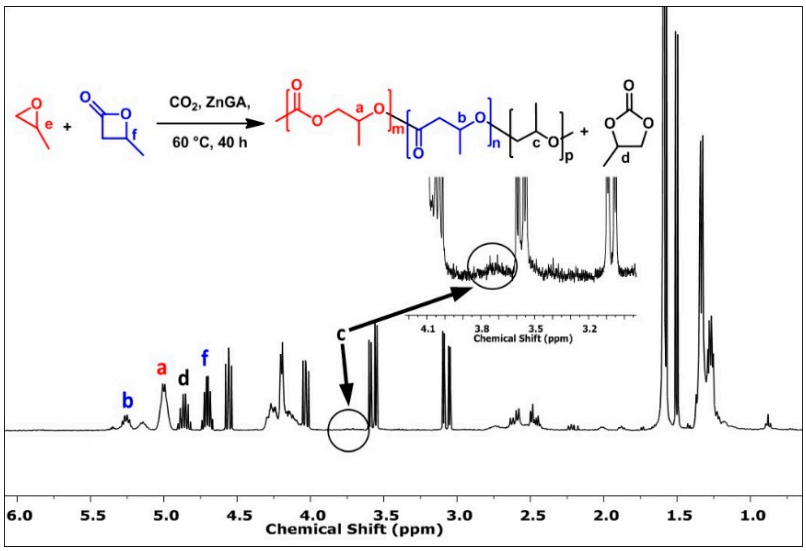



**Figure 2.** $^1$H-NMR spectrum of the mixture of poly(ester-co-carbonate) and cyclic carbonate obtained using the conditions of Entry 1, Table 1.

Thus, the methine protons of PHB, PPC, and PC gave rise to resonances located at 5.4–5.1, 4.8–5.0, and 4.8 ppm, respectively. Moreover, the small hump that can be observed at 5.1 ppm is attributable to random PHB and PPC linkages.

From this spectrum, it can be concluded that a terpolymer of PO, BBL, and $CO_2$ was obtained with a very low turnover number (TON) of 7.3 g polymer/g catalyst (Entry 1, Table 1). Interestingly, this heterogeneous, one-pot system affords methanol-insoluble poly(ester-co-carbonates) with random linkages between PPC and PHB polymers. Following this initial success, the terpolymerization was systematically studied at a substrate to catalyst ratio (S/C) of 100 using different PO:BBL ratios (9:1, 3:1, 1:1, and 1:3). The results obtained are summarized in Table 1, and the $^1$H-NMR spectra of the resulting polymers are shown in Figure S1.

As summarized in Table 1, the TON was found to decrease gradually with an increase the amount of BBL. The highest TON was observed for the infeed PO to BBL ratio of 3:1. Interestingly, the PHB content in the terpolymer increased with the amount of BBL in the feed, reaching a maximum of 29.0% when the feed ratio of PO to BBL was maintained as 1:3 (Entry 5, Table 1). These results suggested that by controlling the PPC/PHB ratio in the resulting polymers, their thermal and mechanical properties might be tuned.

Among the screened reactions, the highest TON of 24.6 g polymer/g catalyst was obtained when the infeed ratio of PO to BBL was 3:1, which afforded lactone and PO conversions of 22.4% and 54.6%, respectively (Entry 3, Table 1). Next, the S/C ratio was increased to 270, a ratio that was used in the regular copolymerization of PO and $CO_2$, and the feed ratio of PO to BBL was set to 0.75:0.25 with 1.5 MPa of $CO_2$.

**Table 1.** Terpolymerization of PO, $CO_2$, and BBL using ZnGA-20 [a].

| Entry | Zn:PO:BBL | $CO_2$ (MPa) | TON [b] | Conversion (%) [c] | | PPC (%) | PHB (%) | PE (%) [d] | $M_n$ (kg/mol) [e] | PDI [e] | $T_g$ (°C) [f] | $T_{5\%}$ (°C) [g] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | PO | BBL | | | | | | | |
| 1 [h] | 1:15:13 | 1.5 | 7.3 | 58.0 | 46.5 | 62.0 | 36.0 | 2.5 | – | – | – | – |
| 2 | 1:90:10 | 1.5 | 24.0 | 47.4 | 21.6 | 93.0 | 4.0 | 3.0 | 69.8 | 3.7 | 37 | 183.4 |
| 3 | 1:75:25 | 1.5 | 24.6 | 54.6 | 22.4 | 87.0 | 10.0 | 3.0 | 45.1 | 3.5 | 34 | 209.9 |
| 4 | 1:50:50 | 1.5 | 18.5 | 58.1 | 12.6 | 82.0 | 15.0 | 2.0 | 41.4 | 4.9 | 30 | 206.1 |
| 5 | 1:25:75 | 1.5 | 9.5 | 48.6 | 8.3 | 67.0 | 29.0 | 3.0 | 25.9 | 5.6 | 20 | 231.9 |
| 6 | 1:202.5:67.5 | 1.5 | 60.8 | 49.4 | 22.4 | 86.0 | 11.0 | 4.0 | 127.5 | 2.5 | 34 | 224.2 |
| 7 | 1:135:135 | 1.5 | 67.5 | 78.5 | 19.3 | 82.0 | 17.0 | 2.0 | 83.5 | 2.6 | 35 | 242.2 |
| 8 | 1:202.5:67.5 | 3.0 | 74.4 | 62.5 | 25.0 | 88.0 | 10.0 | 2.0 | 123.0 | 2.6 | 41 | 212.8 |
| 9 [i] | 1:202.5:67.5 | 15 | na | 0.0 | 0.0 | nd | nd | nd | na | na | na | na |

[a] Reaction condition: 0.05 g of catalyst, 60 °C, and 40 h. [b] TON: g of polymer/g of catalyst, calculated from the resulting polymer. [c] Conversion into the polymeric product. [d] PE = polyether; [e] $M_n$, $M_w$, and polydispersity index (PDI) values of the polymers were determined using gel permeation chromatography (GPC) with polystyrene standards in tetrahydrofuran (THF); PDI = $M_w/M_n$. [f] Obtained via differential scanning calorimetric (DSC) analysis. [g] Obtained via thermogravimetric analysis (TGA) analysis. [h] 0.2 g of ZnGA is used. [i] Reaction was performed in the absence of catalyst; nd = not detected; na = not applicable.

As expected, the TON was found to increase remarkably to 60.8 g polymer/g catalyst, and the corresponding polymer contained PPC and PHB units in an 8:1 ratio (Entry 6, Table 1). The conversions of the monomers PO and BBL reached values similar to those obtained using an S/C ratio of 100, i.e., 49.4% and 22.4%, respectively, thereby demonstrating the catalytic nature of the process. Surprisingly, increasing the BBL content to 50% in feed under similar conditions led to a significant increment in the TON, along with an improvement of the PO conversion to 78.5% (Entry 7, Table 1). Finally, the $CO_2$ pressure also had an influence on the reaction, as can be seen in Entry 8, Table 1. Thus, when the PO to BBL ratio was maintained at 0.75:0.25 with an S/C ratio of 270, increasing the $CO_2$ pressure to 3.0 MPa afforded the highest TON of 74.4, and the PPC to PHB ratio in the resultant polymer was found to be 9:1. Furthermore, the conversion rates of PO and BBL were found to increase to 62.5% and 25%, respectively. Finally, a blank experiment in the absence of catalyst was performed in which no product formation was observed and both PO and BBL were found to remain unchanged after the reaction indicating the true catalytic nature of the reaction (Entry 9, Table 1).

### *2.3. Properties of the Terpolymers*

The terpolymers obtained were subjected to GPC analysis, and the representative GPC elugrams of the terpolymers from Entry 7 and Entry 8 are shown in Figure 3a. Interestingly, broad curves with large PDI values were observed in the elugrams. The unimodal distribution curves show that the polymers were formed as random copolymers of the PPC and PHB units. The small hump at 5.1 ppm in the $^1$H-NMR spectra of the polymers also suggests that the polymers had random PPC and PHB linkages. (Figure 3a and Figure S1). The $M_n$ values of the terpolymers were low when the S/C ratio was maintained at 100, whereas high-molecular-weight polymers were formed in the case of S/C = 270. Moreover, the $M_n$ value was found to increase with the PPC content in the polymers.

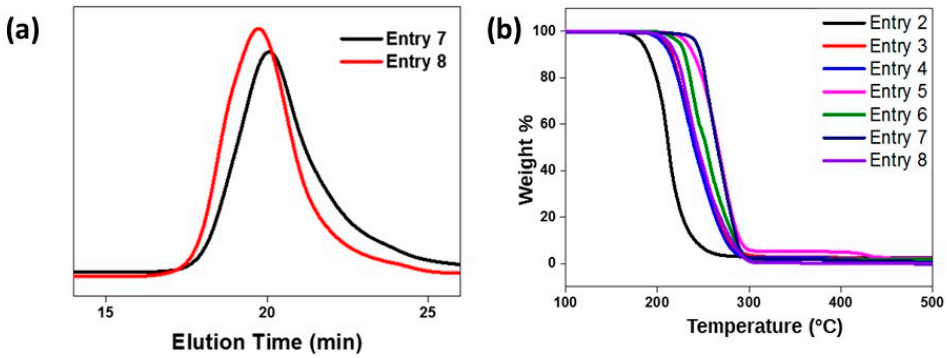



**Figure 3.** (**a**) GPC elugrams of the terpolymers corresponding to Entries 2–8 in Table 1; (**b**) TGA curves of the poly(ester-co-carbonates) obtained from Entries 2–8 in Table 1.

The thermal stability and $T_g$ of the terpolymers were then determined using TGA and DSC analyses. The 5% decomposition temperature values ($T_{5\%}$) for the polymers were obtained from the TGA curves and are listed in Table 1. Figure 3b shows the TGA curves of the obtained polymers corresponding to Entries 2–8 in Table 1. As expected, the thermal stability of the polymers increased with the PHB content. From Entries 6–8, it is evident that the polymer from Entry 7 with higher PHB content shows the highest $T_{5\%}$ value. The $T_g$ value of the terpolymers decreased when the PHB content increased, and the lowest $T_g$ value of 20 °C was obtained for the polymer with the maximum PHB content of 29% (Table 1).

## 3. Materials and Methods

ZnO (99.99%) and BBL (1.25 M) were purchased from Sigma–Aldrich (Seoul, Korea) and were used as received. Glutaric acid (≥99.0%) was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and was used without further purification. Propylene oxide (≥99.9%) was received from Sigma–Aldrich (Seoul, Korea) and was distilled over $CaH_2$ before use. High-purity $CO_2$ gas was obtained from Shinyang Gas Industries (Paju-si, Korea) and was used as received.

The morphologies of the as-prepared catalysts were characterized by field emission scanning electron microscopy (a Hitachi FE-SEM S-4800, Tokyo, Japan). Powder X-ray diffraction (PXRD) measurements were performed at room temperature using a X-Ray Diffractometer system (D/MAX-2500V) Rigaku, (Tokyo, Japan) using CuKα radiation. Fourier-transform infrared (FT-IR) spectra were obtained on a Nicolet iS 50 (Thermo Fisher Scientific, Waltham, MA, USA) spectrometerthat was equipped with an attenuated total reflectance (ATR) accessory at room temperature. Metal content in ZnGA-20 was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) (iCAP-Q, Thermo Fisher Scientific, Waltham, MA, USA) using microwave assisted acid digestion system (MARS6, CEM/USA, (Waltham, MA, USA)). The $N_2$ adsorption–desorption measurements were conducted using an automated gas sorption system (Belsorp II mini, BEL Japan, Inc., Tokyo, Japan) at 77 K. The samples were degassed for 12 h at 130 °C before performing the measurement. The Barrett–Joyner–Halenda (BJH) method was used to

assess the pore size distribution. The $^1$H-NMR spectra of the products were obtained using a Bruker Ascend 400 MHz spectrometer (Rheinstetten, Germany). Thermogravimetric analysis (TGA) was performed using a 2960 Simultaneous DSC-TGA instrument (TA instruments, New Castle, DE, USA) at a heating rate of 10 °C/min from 25 °C to 500 °C under a nitrogen atmosphere. Differential scanning calorimetric (DSC) tests were performed on a PerkinElmer DSC 4000 instrument (Waltham, MA, USA) at a heating rate of 10 °C/min from −40 °C to 120 °C under a nitrogen atmosphere. The molecular weights and polydispersity index of the polymers were determined by gel permeation chromatography (GPC) using a Waters 717plus instrument (Milford, MA, USA) that was equipped with a Waters 515 HPLC pump (Massachusetts, United States). The columns were eluted with THF at a flow rate of 1.00 mL/min at 35 °C. The GPC curves were calibrated using polystyrene standards with molecular weight ranging from 580 to 660,500.

### *3.1. Synthesis of ZnGA-20*

Glutaric acid (1.321 g, 10.0 mmol) and ZnO (0.814 g, 10.0 mmol) were charged into a glass-autoclave reactor followed by 20.0 mL anhydrous toluene under Ar atmosphere. The resulting white suspension was stirred at 20 °C for 24 h. After 24 h, the reaction mixture was filtered off, washed with excess of acetone (50.0 mL × 5), and dried under vacuum at 130 °C to yield 1.910 g of ZnGA-20 (Yield = 97.6%). The content of Zn in the catalyst was estimated to be approximately 33.4 wt.% by ICP-OES.

### *3.2. General Procedure for the Copolymerization of $CO_2$ and PO*

All terpolymerization reactions were carried out in a pre-dried 100 mL stainless steel autoclave reactor equipped with a magnetic stirrer and a programmable temperature controller. In a typical reaction, the desired amounts of catalyst, PO, and BBL were added under Ar atmosphere and then pressurized with $CO_2$ to 1.5 MPa at room temperature. The mixture was stirred at 60 °C for 40 h. After cooling the reactor to room temperature, $CO_2$ was slowly released. A small fraction was taken for $^1$H NMR analysis and the remaining mass was dissolved in dichloromethane (5.0 mL) and was treated with 1.25 M methanolic HCl solution (20.0 mL × 3). Addition of excess methanol (~50.0 mL) to the solution afforded the polymer as a white precipitate and was dried under vacuum at 60 °C for 12 h.

## 4. Conclusions

The terpolymerization of PO, BBL, and $CO_2$ was achieved for the first time using the heterogeneous nano-sized catalyst ZnGA-20. The reactivity of both PO and BBL was found to increase when increasing the $CO_2$ pressure. Furthermore, the polyester incorporation into the poly(carbonate-co-ester), which reached a maximum of 29%, could be tuned by adjusting the feed ratio of PO to BBL. The thermal stability of the terpolymers increased, whereas $T_g$ decreased, when the PHB content increased.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/8/9/393/s1, Figure S1: $^1$H-NMR spectra of the polymers produced using the conditions described in Entries 2–8, Table 1 of the main text. Table S1: PXRD and BET data of ZnGA-20.

**Author Contributions:** Conceptualization, S.P. and S.Y.; Formal Analysis, S.P. and S.D.; Investigation, S.P.; Writing-Original Draft Preparation, S.P.; Supervision, S.Y.

**Acknowledgments:** We acknowledge the financial support through grants from the Korea CCS R&D Center, funded by the Ministry of Education, Science and Technology of the Korean Government (No. 2014M1A8A1049300).

**Conflicts of Interest:** The authors declare no conflict of interest.

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