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Special Issue: Polycarbonates and Green Chemistry

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EDITORIAL

Polycarbonates and green chemistry

S. Guillaume and L. Mespouille, *J. Appl. Polym. Sci.* 2014,
DOI: 10.1002/app.40081

REVIEWS

Porous crystals as active catalysts for the synthesis of cyclic carbonates

M. Zhu and M. A. Carreon, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39738

Renaissance of aliphatic polycarbonates: New techniques and biomedical applications

J. Xu, E. Feng and J. Song, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39822

RESEARCH ARTICLES

Chemical modification of bisphenol A polycarbonate by reactive blending with ethylene carbonate

M. Colonna, C. Berti and M. Fiorini, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39820

Synthesis and characterization of poly(ester carbonate)s by melt-phase interchange reactions of dihydroxy compounds with alkylene and aryene diphenyl dicarbonates containing ester groups

B. A. Sweileh, H. R. Al-Qalawi and H. A. Mohammad, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39904

Terpolymerization of benzyl glycidyl ether, propylene oxide, and CO₂ using binary and bifunctional [rac-SalcyCo^{III}X] complexes and the thermal and mechanical properties of the resultant poly(benzyl 1,2-glycerol-co-propylene carbonate)s and poly(1,2-glycerol-co-propylene carbonate)s

H. Zhang and M. W. Grinstaff, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39893

Synthesis of biodegradable high molecular weight polycarbonates from 1,3-trimethylene carbonate and 2,2-dimethyltrimethylene carbonate

M. Pastusiak, P. Dobrzynski, J. Kasperczyk, A. Smola and H. Janecze, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.40037

Propylene carbonate as a source of carbonate units in the synthesis of elastomeric poly(carbonate-urethane)s and poly(ester-carbonate-urethane)s

M. M. Mazurek, P. G. Parzuchowski and G. Rokicki, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39764

Synthesis and properties of biodegradable multiblock poly(ester-carbonate) comprising of poly(L-lactic acid) and poly(butylene carbonate) with hexamethylene diisocyanate as chain-extender

J. Wang, L. Zheng, C. Li, W. Zhu, D. Zhang, G. Guan and Y. Xiao, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39158

Effect of interfacial tension on the cell structure of poly(methyl methacrylate)/bisphenol A polycarbonate blends foamed with CO₂

P. Gong and M. Ohshima, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39228

Flame retardancy and thermal properties of carboxyl-containing polysiloxane derivatives in polycarbonate

R. Song, L. Chang and B. Li, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39814

Clay-induced degradation during the melt reprocessing of waste polycarbonate

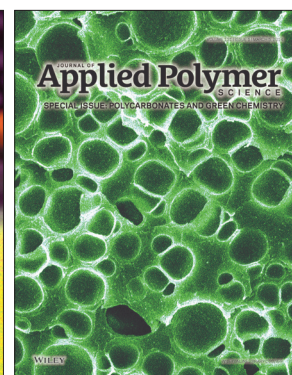
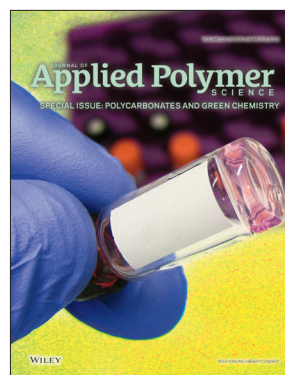
M. U. de la Orden, D. P. C. Muñoz, V. Lorenzo and J. M. Urreaga, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39997

Preparation and properties of polycarbonate microspheres containing tetanus toxoid vaccine

B. Hu, X.-J. Ke, G.-P. Yan, R.-X. Zhuo, Y. Wu, C.-L. Fan and Y.-J. Liu, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.40048

New thermogelling poly(ether carbonate urethane)s based on pluronics F127 and poly(polytetrahydrofuran carbonate)

X. J. Loh, H. X. Gan, H. Wang, S. J. E. Tan, K. Y. Neoh, S. S. J. Tan, H. F. Diong, J. J. Kim, W. L. S. Lee, X. Fang, O. Cally, S. S. Yap, K. P. Liong and K. H. Chan, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/app.39924



Terpolymerization of Benzyl Glycidyl Ether, Propylene Oxide, and CO₂ Using Binary and Bifunctional [*rac*-SalcyCo^{III}X] Complexes and the Thermal and Mechanical Properties of the Resultant Poly(benzyl 1,2-glycerol-co-propylene carbonate)s and Poly(1,2-glycerol-co-propylene carbonate)s

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ABSTRACT: The terpolymerization of benzyl glycidyl ether (BGE), propylene oxide (PO), and CO₂ using both a binary [*rac*-SalcyCo^{III}DNP]/PPNDNP system and a bifunctional [*rac*-SalcyCo^{III}DNP] catalyst bearing a quaternary ammonium salt is reported. Catalyst activities range from 149 to 563 h⁻¹ for the binary catalyst at the various monomer feeding ratios. The bifunctional catalyst shows increased activity up to 857 h⁻¹ at higher temperature with slightly compromised polymer selectivity. The percentage of BGE or PO incorporation in the polymer chain reflects the initial feeding ratio and remains constant during the course of the reaction. A Fineman-Ross plot determined the monomer reactivity ratio to be 1.15 and 0.93 for BGE and PO, respectively. The glass transition temperature of the terpolymers is dependent on 1,2-glycerol carbonate (GC) content and decreases from 37 to 8°C with increasing GC content. The decomposition temperature at 5% weight loss also shows a similar dependency, and varies from 233 to 269°C. The benzyl protecting group is removed using H₂ and Pd/C to afford the poly(1,2-glycerol-co-propylene carbonate)s (PGC-co-PC). The glass transition and decomposition temperatures as well as the mechanical properties are lower for the PGC-co-PCs compared with the corresponding values for the poly(benzyl 1,2-glycerol-co-propylene carbonate)s. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39893.

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INTRODUCTION

Polycarbonates are versatile polymers used in a wide range of applications spanning from the electronic to the biomedical arena because of their favorable temperature resistance, impact resistance, degradation, and optical properties.¹ Traditionally, polycarbonates are prepared via the polycondensation of diols with phosgene, and, although extensively used, this method does possess drawbacks.² The catalytic approach to couple CO₂ with an epoxide in an alternating fashion represents one of the most promising and environmental-friendly methods to synthesize polycarbonates. With the discovery of the [SalcyCo^{III}X] catalyst for the polymerization,³ a series of highly active and selective catalyst systems are reported including those based on the binary [SalcyCo^{III}X]/PPNY system.^{4–9} These cobalt metal complexes are active copolymerization and terpolymerization catalyst for a variety of cyclic and acyclic aliphatic epoxides with CO₂.^{10–14}

Of the various available cyclic and acyclic aliphatic epoxides, our interest is in those monomers that yield a 1,2-linked glycerol carbonate (GC) unit as the polymer backbone. Glycerol is a natural metabolite found in the human body and is a component in lipid structures. It possesses favorable biodegradation and biocompatible properties and is found on the FDA GRAS list.¹⁵ Consequently, glycerol based polymers are being investigated for a number of biomedical and pharmaceutical applications including as drug loaded buttressing films,¹⁶ particles for drug delivery,^{17–19} and coatings for prevention of seroma.²⁰ Various polymer architectures ranging from linear to dendritic are reported for pure polyglycerol ethers and carbonates as well as copolymers with hydroxyacids, for example, to give polyether esters or polycarbonate esters.^{21–27} In general, these polymers possess certain advantages including: (1) a pendent primary hydroxyl group for further modification; (2) a biodegradation

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pathway to afford nontoxic and nonacidic products – glycerol and CO₂; and (3) physical properties ranging from amorphous to semicrystalline depending on the polymer or copolymer composition.

Recently, we reported a facile and efficient method to access structurally new glycerol-derived polymers poly(1,2-glycerol carbonate)s by copolymerizing benzyl glycidyl ether (BGE) with CO₂ using [SalcyCo^{III}X] complexes.²⁸ Both atactic and isotactic polymers can be prepared and subsequently deprotected to afford poly(1,2-glycerol carbonate) copolymers composed of only CO₂ and glycerol. With this success, it is now important to extend this methodology to terpolymerizations and to explore the properties of the resultant polymers. Given the significant knowledge on the synthesis and characterization of poly(propylene carbonate)s, we selected propylene oxide (PO) as the third monomer for the terpolymerization with BGE. Poly(propylene carbonate) possesses relatively high impact resistance and scratch resistance properties with a T_g of $\sim 40^\circ\text{C}$, and is a conventional engineering plastic. It is used in a number of industrial and food products, such as coatings for metal food cans due to its excellent oxygen barrier property. In contrast, poly(benzyl 1,2-glycerol carbonate), PBGC, is a soft material and has a low glass transition temperature (T_g) of $\sim 9^\circ\text{C}$. These two monomers when polymerized with CO₂ should give distinct polymers with significantly different properties (e.g., thermal, mechanical) from their respective copolymers. The results gathered from this terpolymerization study will provide insight into the varied polymers that can be obtained with BGE, and into the corresponding structure-property relationships. While terpolymerizations of various (cyclic) aliphatic epoxides such as hexene oxide, butene oxide, cyclohexene oxide with PO and CO₂ are reported,^{10–12} to the best of our knowledge, the terpolymerization of glycidyl ether, PO, and CO₂ is not described. In this work, we report the terpolymerization of BGE, PO, and CO₂ using both binary and bifunctional [*rac*-SalcyCo^{III}X] catalysts, and the thermal and mechanical properties of the resultant poly(benzyl 1,2-glycerol-*co*-propylene carbonate)s and poly(1,2-glycerol-*co*-propylene carbonate)s (PGC-*co*-PC).

EXPERIMENTAL

General Information

CO₂ gas (research grade) was dried through storage in a column of 3 Å molecular sieves at a pressure of 500 psi. PO and BGE were dried by stirring over CaH₂ for a couple of days and vacuum-distilled into a pre-dried flask filled with 3 Å molecular sieves. The ¹H and ¹³C NMR (500 MHz) spectra were recorded on a Variant 500. The size exclusion chromatography (SEC) data was obtained at room temperature in THF [for poly(benzyl 1,2-glycerol-*co*-propylene carbonate)] or in DMF (for PGC-*co*-PC) calibrated against polystyrene standards. The [SalcyCo^{III}X] Catalyst 1 and 2 were prepared following the reported methods.^{6,9}

Representative Procedures for Thermal Measurements

Thermal gravimetric analysis (TGA) measurements were performed on Thermal Analysis TGA Q50. All samples were heated from 20 to 400°C at a heating rate of 20°C/min. Differential scanning calorimetry (DSC) measurements were performed on

Thermal Analysis DSC Q10 at a heating rate of 10°C/min and a cooling rate of 10°C/min from -40 to 200°C for poly(benzyl 1,2-glycerol-*co*-propylene carbonate) and from -40 to 60°C for PGC-*co*-PC. All samples were between 5 and 10 mg by mass, scanned for three heat-cool cycles, and the T_g data was determined from the second heating trace.

Representative Procedure for Rheological Measurement

Rheological measurements were performed on an AR 1000 controlled strain rheometer from TA Instruments equipped with a Peltier temperature control using a 12 mm diameter parallel stainless steel plate. The samples were first made into a ~ 12 mm diameter disk before measurement. The gap was set to be 0.8–1.2 mm in all the runs. Prior to each test, a preshear was done at shear rate 100 s^{-1} for 10 s to eliminate the physical memory of the sample, followed by a 10 min equilibrium step at 37°C in order for the sample to reach a steady-state condition. A strain amplitude of 0.6% was determined to lie within the linear viscoelastic region via an oscillatory strain sweep from 1 to 10 Hz.

A Representative Terpolymerization Procedure

An autoclave was assembled inside a glovebox and Catalyst 1 (19.7 mg, 0.025 mmol), PPNDNP (18.0 mg, 0.025 mmol), BGE (1.9 mL, 12.5 mmol), and PO (0.875 mL, 12.5 mmol) were loaded. The autoclave was removed out of glovebox with the valve closed. Next, the reactor was immersed in a 25°C oil bath and CO₂ gas was pressurized to 220 psi and the polymerization reaction run for 2.5 h. The autoclave was then cooled by immersion in an ice bath. Following the release of CO₂, a small amount of the residue was taken and dissolved in CDCl₃ for ¹H NMR analysis to give quantitatively the activity and selectivity of polymer as well as carbonate linkage. The crude terpolymer was dissolved in 6 mL of DCM/MeOH (5/1, v/v) mixture and precipitated from methanol. This process was repeated 4–5 times to completely remove the catalyst and unreacted epoxide. A white polymer was obtained upon vacuum drying.

A Representative Debenzylation Procedure

An autoclave was loaded with poly(benzyl 1,2-glycerol-*co*-propylene carbonate) with 53% BGE (103 mg, 0.33 mmol) and 10% Pd/C (50% water content; 82 mg, 0.033 mmol based on Pd), EtOAc : MeOH = 3 : 1 (4 mL). The autoclave was immersed into a 40°C prewarmed oil-bath and pressurized to 500 psi H₂. After 12 h, the H₂ was slowly released and the solution was filtered through a pad of celite, the residue on the celite was washed with EtOAc : MeOH = 3 : 1, the filtrate was collected, rotovaped, and further dried on vacuum.

NMR for Poly(benzyl 1,2-glycerol-*co*-propylene carbonate) with 53% BGE Unit. ¹H NMR (500 MHz, CDCl₃, δ): 7.20–7.40 (br, 5H, Ar H), 5.00–5.14 [br, 1H; CH(GC)], 4.91–5.00 [br, 1H, CH (PC)], 4.01–4.62 [br, 6H, CH₂ (on backbone + benzyl CH₂)], 3.54–3.73 [br, 2H, CH₂ (side chain)], 1.19–1.42 (br, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃, δ): 154.2, 137.5, 128.4, 127.8, 127.6, 74.3, 73.4, 72.4, 69.2, 69.0, 67.7, 66.2, 16.2.

NMR for PGC-*co*-PC with 53% BGE Unit. ¹H NMR (500 MHz, CDCl₃, δ): 5.01–5.13 (br, 1H, OH), 4.84–4.95 [br, 1H; CH(GC)], 4.73–4.84 [br, 1H; CH(PC)], 4.01–4.41 [br, 4H, CH₂

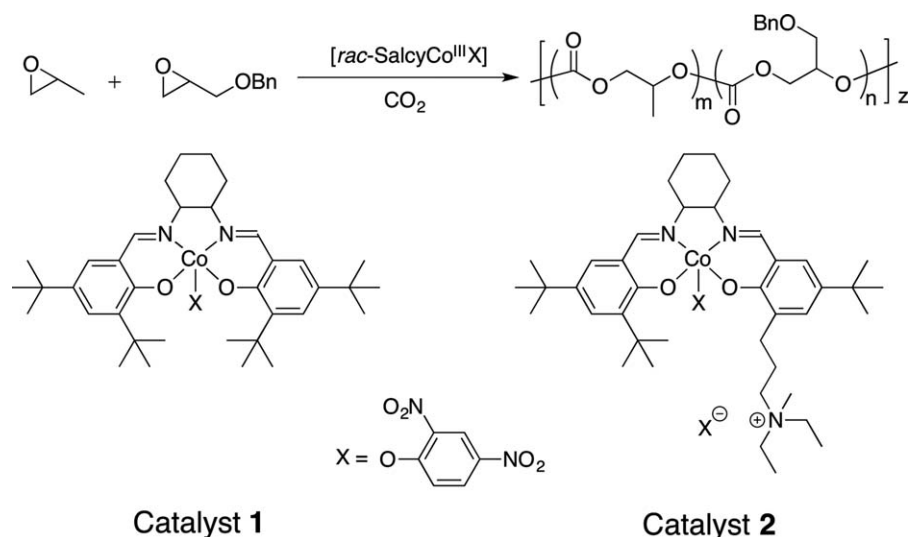


Figure 1. Terpolymerization of BGE, PO, and CO₂ using [*rac*-SalcyCo^{III}X] binary and bifunctional complexes **1** and **2**, respectively.

(on backbone)], 3.45–3.64 [br, 2H, OCH₂ (side chain)], 1.14–1.32 (br, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃, δ): 154.3, 154.1, 76.8, 72.8, 69.2, 66.4, 59.6, 55.3, 16.1.

RESULTS AND DISCUSSIONS

Both the binary system of [*rac*-SalcyCo^{III}X]/PPNY (**1**) and the bifunctional [*rac*-SalcyCo^{III}X] complex (**2**) bearing a quater-

nary ammonium salt side arm on the 3-position of the aromatic ring catalyze the terpolymerization of BGE, PO, and CO₂ (Figure 1 and Table I). The binary catalyst system (**1**) exhibited good activity towards the terpolymerization of BGE, PO, and CO₂ at various monomer feeding ratios to afford polycarbonates with high polymer and carbonate linkage selectivities (>99%) as well as narrow polydispersities (*M_w/M_n*; Table I, Entries 1–9). Catalyst activities [turn over

Table I. Results from the Terpolymerization of BGE, PO, and CO₂^a

#	Catalyst	<i>f</i> _{BGE} ^b	<i>F</i> _{BGE} ^c	Temp (°C)	Turnover freq. (h ⁻¹)	Time (h)	Polymer selectivity (%)	<i>M_n</i> ^d (kg/mol)	PDI ^d (<i>M_w/M_n</i>)	<i>T_g</i> (°C)	<i>T</i> _{decomp} 5/50 (%) ^e
1	1	1.00	1.00	25	149	4.0	>99	15.4	1.13	8	269/304
2	1	0.80	0.82	25	170	4.0	>99	19.3	1.14	11	259/297
3	1	0.60	0.63	25	225	3.0	>99	18.0	1.15	15	260/294
4	1	0.50	0.52	25	318	0.5	>99	5.2	1.11	N.D.	N.D.
5	1	0.50	0.52	25	301	1.25	>99	11.8	1.14	N.D.	N.D.
6	1	0.50	0.53	25	245	2.5	>99	17.9	1.16	19	258/291
7	1	0.40	0.42	25	296	2.5	>99	20.8	1.15	21	240/281
8	1	0.20	0.22	25	404	1.5	>99	17.0	1.16	25	232/267
9	1	0	0	25	563	1.25	>99	24.1	1.13	37	233/265
10	1	0.50	0.50	50	456	1.5	70	11.8	1.13	N.D.	N.D.
11	2	0.50	0.58	25	330	12	>99	28.4	1.18	N.D.	N.D.
12	2	0.50	0.60	40	520	8.0	>99	28.8	1.18	N.D.	N.D.
13	2	0.50	0.60	60	789	5.0	98	27.3	1.17	N.D.	N.D.
^f 14	2	0.50	0.60	60	857	5.0	98	32.3	1.19	N.D.	N.D.

^a All reactions were performed in neat BGE + PO (25 mmol in total) in a 15 mL autoclave under 220 psi of CO₂ pressure with 1000 : 1 : 1 (for # 1–9) or 6000 : 1 (for # 10–11) substrate/*rac*-SalcyCo^{III}DNP/PPNDNP loading at 25°C. All resultant poly(benzyl 1,2-glycerol-co-propylene carbonate)s [poly(BGC-co-PC)] contain >99% carbonate linkage and >99% polymer selectivity, determined by ¹H spectroscopy.

^b Molar fraction of BGE in the substrate.

^c Molar fraction of BGE in the resultant poly(BGC-co-PC).

^d Determined by SEC using polystyrene as standards. All resultant polycarbonates showed bimodal distribution, the molecular weights are averaged over two peaks.

^e The temperature at 5 and 50% weight loss, respectively, on the TGA curve of the copolymers.

^f The reaction was run under 440 psi.

N.D. = not determined.

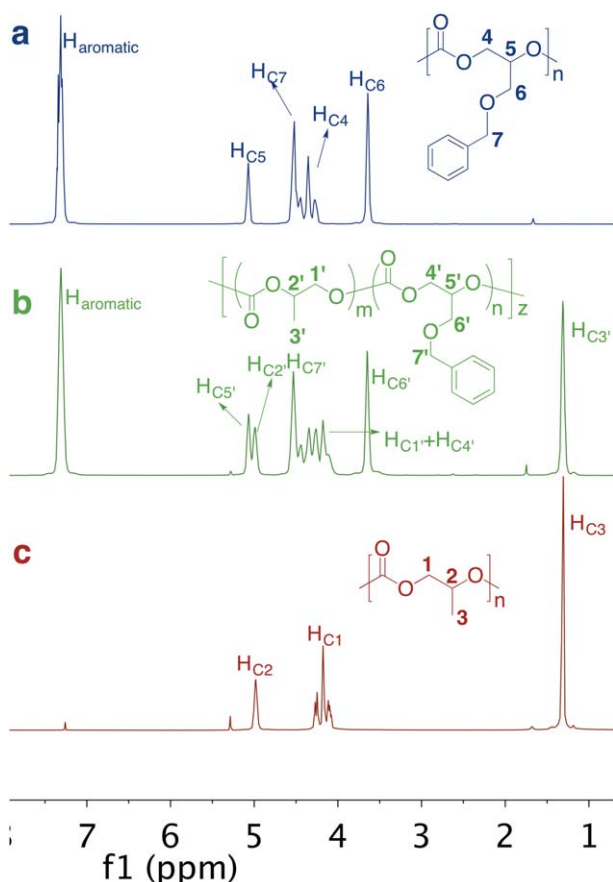


Figure 2. Representative ¹H NMR Spectra of (a) poly(benzyl 1,2-glycidyl carbonate); (b) poly(benzyl 1,2-glycerol-co-propylene carbonate) with 53% GC units, and (c) poly(propylene carbonate). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

frequency, TOF (h⁻¹)] were negatively correlated to the BGE feeding ratio and were 149 h⁻¹ for pure BGE and 550 h⁻¹ for pure PO, which were in good agreement with previous results.^{4,6,28} Increasing the temperature from 25 to 50°C resulted in greater catalyst activity from 245 to 456 h⁻¹. Polymer selectivity, however, was significantly compromised (70%; Table I, Entry 10). The selectivities for formation of PBGC and poly(propylene carbonate) (PPC) units over their corresponding cyclic carbonates were 65 and 74%, respectively, whereas the selectivities were 87 and 95% for pure BGE and PO polymers under the same reaction condition.^{6,28}

Based on these results, we also investigated the bifunctional [*rac*-SalcyCo^{III}DNP] complexes (catalyst 2) bearing a quaternary ammonium salt on the ligand framework of the catalyst, since this catalyst is known to be stable and active even under high temperature and in diluted solution.⁹ Cobalt complex 2 efficiently catalyzed the terpolymerization under low catalyst loading and even at elevated temperature without compromising the polymer selectivity (Table I, Entry 11–13). For example, a TOF of 330 h⁻¹ was observed with BGE : PO = 1 : 1 under 6000 : 1 catalyst loading at 25°C (Table I, Entry 11). As before, increasing the temperature to 40°C afforded a significant increase in TOF to 520 h⁻¹. The highest activity of 857 h⁻¹ was achieved at 60°C with a slight compromise in polymer selectivity (98%).

The ¹H NMR spectra showed clearly separated peaks at δ = 5.0 attributed to the CH in 1,2-glycerol carbonate (GC) units (δ = 5.07) and propylene carbonate (PC) units (δ = 4.99) in the polymer chain. No peak was observed at δ = 3.4–3.5, which verified the high carbonate linkage over ether linkage selectivity (>99%) [Figure 2(b)]. The polymers were soluble in solvents such as dichloromethane, chloroform, ethyl acetate, and DMF.

Due to the absence of the ether linkage in the polymer backbone the terpolymerization can be treated as the copolymerization of the two monomeric carbonate units. The methine protons corresponding to the monomeric units in the polymer backbone of the terpolymer (δ = 5.07, 4.99) were clearly separated in the ¹H NMR spectra, but not resolved enough to directly calculate each monomeric unit content [Figure 2(b)]. However, the isolated methylene signal at δ = 3.65 for the methylene group connected to the benzyloxy group, enabled us to calculate the percentage of each monomeric unit present in the terpolymer. These calculations revealed that the percentage of benzyl 1,2-glycerol carbonate unit in the polymer closely matched the initial feeding ratio of the two monomers, and that the percentage remained constant during the course of the

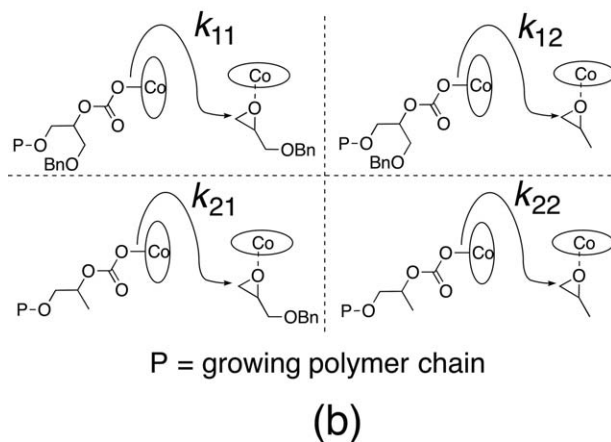
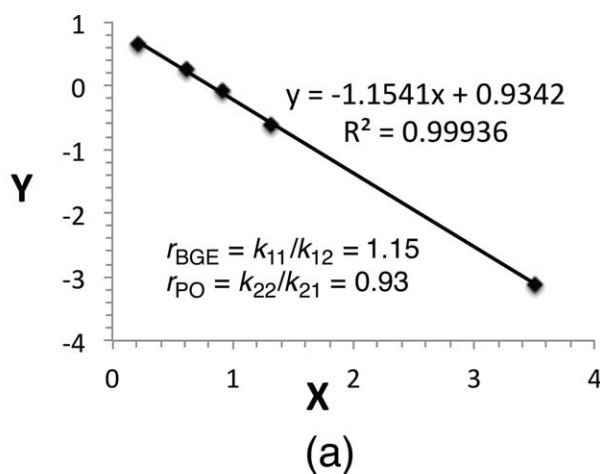


Figure 3. (a) Fineman-Ross plot for the terpolymerization ($Y = \{f_{BGE}/(1 - f_{BGE})\}\{(1 - 2f_{BGE})/F_{BGE}\}$; $X = \{f_{BGE}^2/(1 - f_{BGE})^2\}\{(1 - F_{BGE})/F_{BGE}\}$). (b) Schematic presentation of kinetic parameters during the chain propagation.

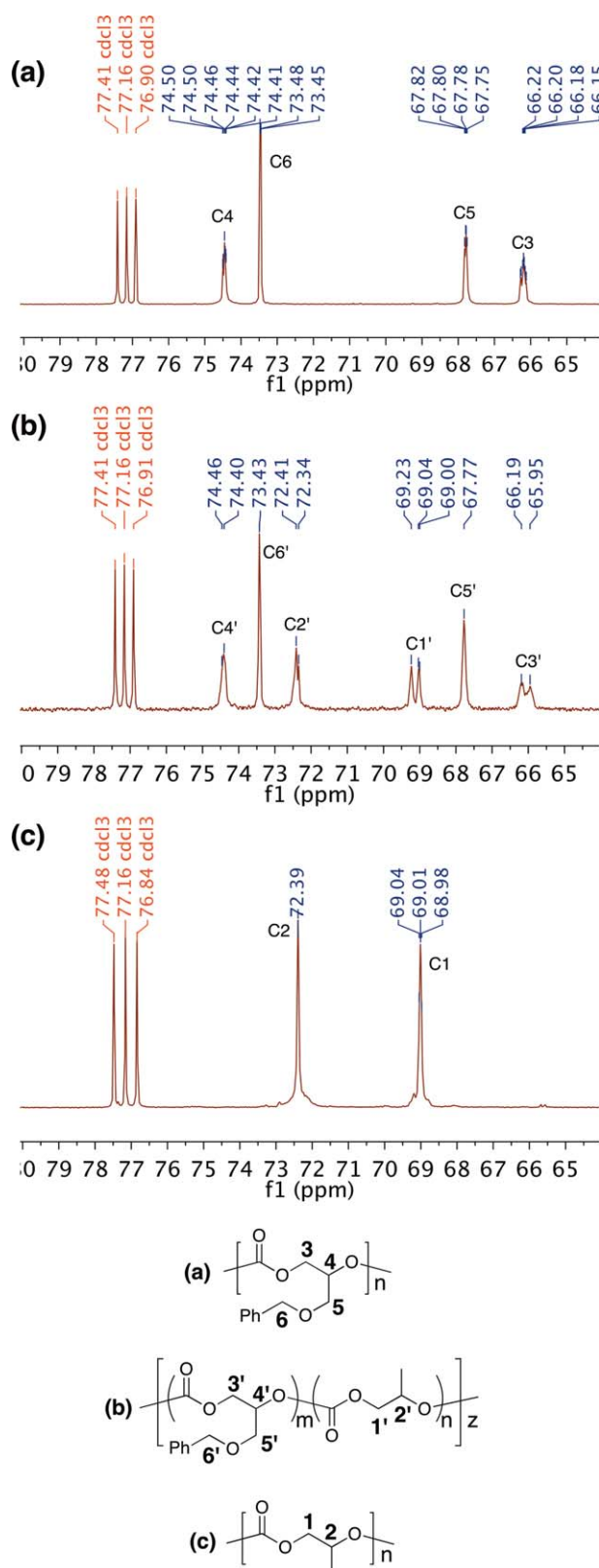


Figure 4. ^{13}C Spectra of (a) PBGC, (b) poly(benzyl 1,2-glycerol-co-propylene carbonate), and (c) poly(propylene carbonate). Note: Please see assignment in Supporting Information. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction (Table I, Entries 4–6) for the binary [*rac*-Salcy-Co^{III}DNP]/PPNDNP catalyst, **1**. For the bifunctional Catalyst, **2**, even a higher percentage of the benzyl 1,2-glycerol carbonate unit was incorporated than the initial monomer feeding ratio (Table I, Entries 11–13). This result is interesting since: (1) PO is almost four times more reactive than BGE with the binary catalyst system (Table I, Entries 1 and 9); and (2) previous reports describing the terpolymerization of hexene oxide/butene oxide/cyclohexene oxide with PO and CO₂ showed the percentage of incorporation for the less reactive, cyclic aliphatic epoxide to be lower than their initial feeding ratio.¹²

The data for the mole fraction of BGE in the feed and the 1,2-glycerol carbonate (GC) unit in the polymer fit the Fineman-Ross plot with a high correlation ($R^2 = 0.999$) (Figure 3). The monomer reactivity ratio of BGE ($r_{\text{BGE}} = k_{11}/k_{12}$) and PO ($r_{\text{PO}} = k_{22}/k_{21}$) were determined to be 1.15 and 0.93, respectively. These results indicate that the consecutive incorporation of two PO units is slightly unfavored.

The ^{13}C spectra of PBGC, PBGC-co-PC, and PPC were studied and compared. As shown in Figure 4, the ^{13}C spectrum of PBGC-co-PC was more than the simple sum of the PBGC and PPC spectra, for example, the C1 in the PPC and the C3 in the PBGC showed obvious splitting in the terpolymer compared with their respective copolymer, while C5 in PG showed four small splitting and exhibited only one peak in the terpolymer. This result indicates that the GC and PC units did not form long block sequences. We cannot experimentally determine if the sequence is purely alternating. Given that the reactivity ratio of BGE and PO are close to 1 and that the value remained constant during the course of the reaction, the random terpolymer follows Bernoullian statistics with a probability (P) close to 0.5. It likely consists of alternating GC and PC units, as well as a statistical distribution of di-, tri-, tetra-, penta-, and so on homo-oligo GC and PC sequences interspersed along the polymer chain.

The glass transition temperature (T_g) and decomposition temperature (T_{decomp}) were also studied for the resultant polymers. The T_g of pure PBGC and PPC were determined to be 8 and 37°C, respectively (Table I, Entries 1 and 9). The lowered T_g for PPC compared to the reported result (42°C) is likely due to the low molecular weight (24 vs. 62 kg/mol).¹¹ It is worth noting that incorporation of GC has a significant impact on T_g . For example, 22% GC incorporation resulted in a sharp decrease of polymer T_g from 37 to 25°C, while further increases in the PBGC content from 22 to 100% afforded a steady decrease in T_g from 25 to 8°C.

The $T_{\text{decomp}50\%}$ increased from 233°C for pure poly(propylene carbonate) to 269°C for pure PBGC with increasing GC unit percentage. The $T_{\text{decomp}50\%}$ showed a similar trend ranging from 265 to 304°C.

Next, the benzyl group in the copolymer was removed via hydrogenation.^{28–30} The terpolymer possessing 53% GC unit ($M_n = 17.9$ kg/mol, Table I, Entry 6) was dissolved in EtOAc : MeOH = 3 : 1 and the reaction was run at 40°C under 500 psi H₂ for 12 h. The ^1H NMR spectrum, in DMSO-*d*₆, showed the disappearance of the signal in the aromatic region ($\delta = 7.2$) for

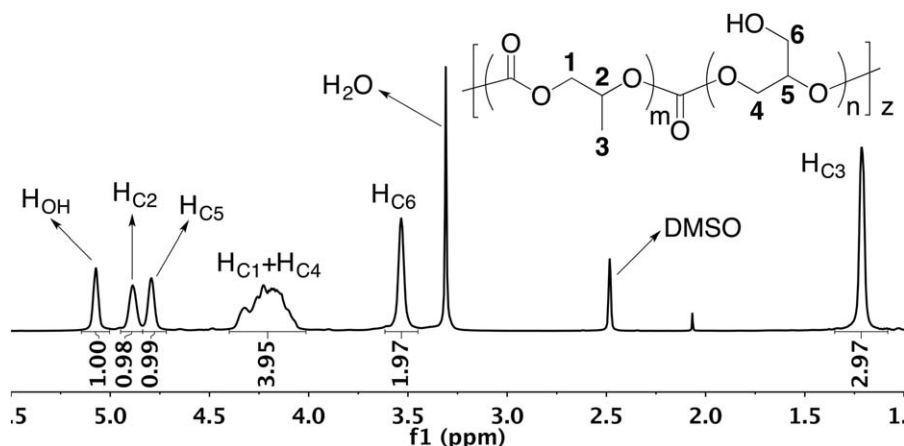


Figure 5. ^1H NMR spectrum of PGC-*co*-PC with 53% GC unit in $\text{DMSO-}d_6$. Note: The counter-intuitive assignment of $\text{H}_{\text{C}2}$ and $\text{H}_{\text{C}5}$ was accomplished by analyzing a known deprotected polymer with 60% GC unit.

the benzyl group, confirming the removal of the primary hydroxyl protecting group (Figure 5). Surprisingly, by deprotecting a known polymer that has 60% GC content, the methine proton belongs to GC unit, which used to be more down-field in CDCl_3 was determined to be more up-field than the methine proton of propylene carbonate in the deprotected polymer in $\text{DMSO-}d_6$ (Figure 5). The deprotected polymers were soluble in polar solvents such as DMF and DMSO or mixed solvent system such as $\text{EtOAc} : \text{MeOH} = 3 : 1$. SEC in DMF calibrated against polystyrene standards indicated the molecular weight (M_n) of the resultant polymer to be 11.8 kg/mol, consistent with its structure, indicating that the polymer backbone remained intact during the reaction. The deprotected polymer ($M_n = 17.3$ kg/mol, from Table I, Entry 12) with 60% of GC unit showed a T_g of 10°C , which is 5°C lower than the protected version of the same molecular weight (Table I, Entry 3). $T_{\text{decomp}5\%}$ and $T_{\text{decomp}50\%}$ were determined to be 162 and 206°C , respectively. However, we suspect that chain scission can occur at a lower temperature than the $T_{\text{decomp}5\%}$ and, thus, we performed a second T_g experiment. If we increase the isotherm temperature from 60 to 100°C , the T_g decreases from 10 to 4°C . No peaks were detected in the measured range (down to -40°C) when the isotherm temperature was further increased to 150°C , at which temperature there was also no significant weight loss when the sample was analyzed by TGA analysis. These results indicate that chain scission occurs at elevated temperatures (150°C) resulting in a significant decrease in T_g .

Rheological studies on cast molds of the polymers showed that PBGC, poly(benzyl 1,2-glycerol-*co*-propylene carbonate) (PBGC-*co*-PC) and the deprotected PGC-*co*-PC exhibited tough mechanical properties. As shown in Figure 6, in the 1–3 Hz region the storage modulus (G') and loss modulus (G'') of the PBGC with a molecular weight of 30.3 kg/mol ranged from 2.0×10^5 to 3.4×10^5 Pa and 2.0×10^5 to 3.8×10^5 Pa, respectively. Incorporation of 40% of propylene carbonate unit in the polymer chain ($M_n = 32.3$ kg/mol) resulted in a ~ 7 times increase in both G' and G'' . Compared with the protected version, the debenzylated copolymer PGC-*co*-PC

(60% GC, $M_n = 17.3$ kg/mol) showed a lowered G' and G'' , and the values ranged from 4.37×10^5 to 9.51×10^5 Pa and 5.21×10^5 to 1.14×10^6 Pa, respectively. However, these values were still 2–3 times greater than those measured for pure PBGC.

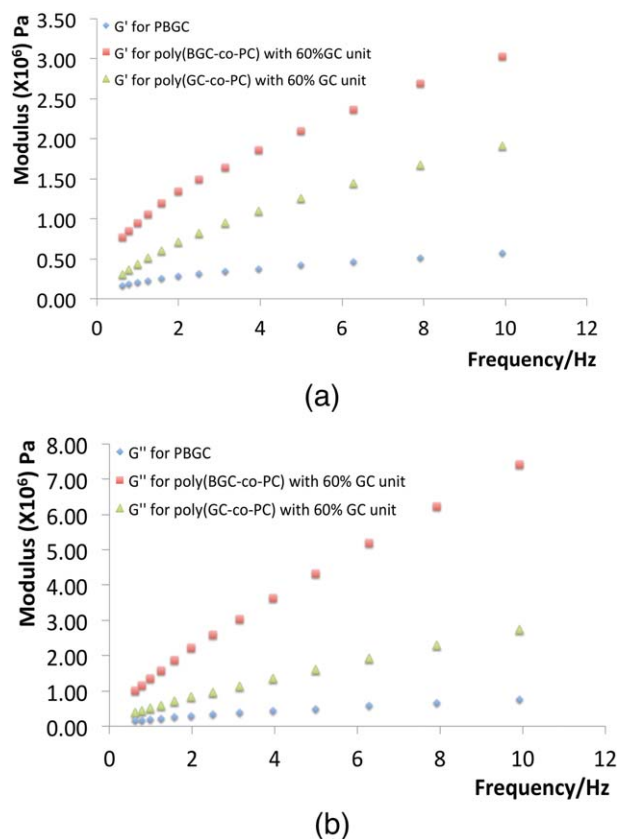


Figure 6. Rheological properties of (a) shear storage modulus (G') and (b) shear loss modulus (G'') of PBGC, $M_n = 30.3$ kg/mol, poly(benzyl 1,2-glycerol-*co*-propylene carbonate) [poly(BGC-*co*-PC)] with 60% GC unit, $M_n = 32.3$ kg/mol and PGC-*co*-PC with 60% GC unit, $M_n = 17.3$ kg/mol at 25°C . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

The terpolymerization of BGE, PO, and CO₂ is catalyzed by both the binary [*rac*-SalcyCo^{III}DNP]/PPNDP (**1**) and the bifunctional [*rac*-SalcyCo^{III}DNP] (**2**) catalysts with high selectivity. High catalyst activities are observed with activities ranging from 149 to 563 h⁻¹ for Catalyst **1** and 330 to 857 h⁻¹ for Catalyst **2** at various monomer feeding ratios. The bifunctional Catalyst, **2**, exhibited increased activity at higher temperatures without a compromise in polymer selectivity. The percentage of BGE incorporation in the polymer chain closely reflected the initial feeding ratio. This result is in contrast to the reports with less reactive aliphatic epoxides such as butene oxide or cyclohexene oxide where the percentage of incorporation is significantly lower than their initial feeding ratio. The Fineman-Ross plot determined the monomer reactivity ratio to be 1.15 and 0.93 for BGE and PO, respectively. The *T*_g for the resultant copolymers ranged between 37 and 8°C with increasing BGE content and all of the polymers possessed a *T*_{decomp} 5% above 233°C. The benzyl protecting group is removed using H₂ and Pd/C to afford the PGC-*co*-PCs. The glass transition and decomposition temperatures as well as the mechanical properties are lower for the PGC-*co*-PCs compared with the corresponding values for the poly(benzyl 1,2-glycerol-*co*-propylene carbonate)s. BGE is an active monomer for the CO₂ copolymerization with [SalcyCo^{III}X] complexes, and it can be terpolymerized with PO, a structurally and electronically different monomer. These results demonstrate that terpolymers containing glycerol with varied polymer compositions and properties can be efficiently synthesized, and encourages the continued investigation of 1,2-glycerol carbonate based polymers and copolymers from both a basic science as well as an application perspective.

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