

Chopping high-molecular weight poly(1,4-butylene carbonate-co-aromatic ester)s for macropolyol synthesis

Geun Ho Park, Seul Lee, Su Hyun Park, Seong Chan Eo, Jin Gu Kim, Bun Yeoul Lee

Department of Molecular Science and Technology, Ajou University, Suwon 443-749, Korea

Correspondence to: B. Y. Lee (E-mail: bunyeoul@ajou.ac.kr)

ABSTRACT: The condensation of a mixture of dimethyl carbonate and phthalate derivatives with 1,4-butanediol (BD), catalyzed by sodium alkoxide, generated high-molecular weight poly(1,4-butylene carbonate-co-aromatic ester)s with molecular weights (M_n) of 50–120 kDa. The subsequent addition of polyols [BD, glycerol propoxylate, 1,1,1-tris(hydroxymethyl)ethane, or pentaerythritol] chopped these high-molecular weight polymers to afford macrodiols or macropolyols with facile control of their molecular weights (M_w , 2000–3000 Da) and unique chain topological compositions. Macropolyols prepared by chopping poly(1,4-butylene carbonate-co-terephthalate) were waxy in nature, whereas those containing isophthalate and phthalate units were oily. The macropolyols synthesized by this chopping method may have potential applications in the polyurethane industry. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43754.

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INTRODUCTION

The utilization of carbon dioxide is an issue being addressed in both the academic and industrial fields.^{1–4} One method that is currently under investigation for the useful consumption of CO₂ involves its copolymerization with propylene oxide or ethylene oxide to form aliphatic polycarbonates.^{5–14} Alternatively, CO₂ can be reacted to form dimethyl carbonate (DMC), which is subsequently converted to diphenyl carbonate and further to the conventional aromatic polycarbonate.¹⁵ The former process is currently undergoing commercialization, whereas the latter is already under operation industrially.¹⁶ Previously, DMC was produced from extremely toxic phosgene and was considered a harmful chemical, but now, it is recognized as green and inexpensive because of its production from CO₂ or CO.¹⁷ Recently, we reported the synthesis of high-molecular weight poly(1,4-butylene carbonate-co-terephthalate) using the benign DMC.^{18–22} Poly(1,4-butylene carbonate-co-terephthalate) shows attractive properties, such as biodegradability and a melting point (T_m) above 100 °C. However, poly(propylene carbonate) and poly(ethylene carbonate) produced directly by CO₂/epoxide copolymerizations are amorphous polymers, which limits their widespread applications.

Aliphatic polycarbonate-based macropolyols with molecular weights of several thousands are also materials of commercial interest,^{23–27} particularly in the bulk polyurethane (PU) industry, when they are reacted with di(or poly)isocyanates.^{28,29} The

development of environment friendly PUs, such as bio-based, biodegradable, and nonisocyanate PUs, is an issue currently being addressed by scientists.^{30–33} Aliphatic polycarbonate-based macropolyols can be synthesized by either CO₂/epoxide copolymerizations, or by the polycondensation of α,ω -alkanediols with DMC. Aliphatic polycarbonate-based macropolyols are attractive due to their hydrolytic stability and resistance to sunlight and oxidative degradation.^{34,35} Recently, we reported the syntheses of macropolyols with unique chain compositions by chopping high-molecular weight poly(1,4-butylene carbonate)s (PBC) with a diol or polyol.³⁶ In this paper, we report the preparation of a further type of macropolyol by the chopping of high-molecular weight poly(1,4-butylene carbonate-co-aromatic ester)s. Aromatic ester units were incorporated into these macropolyols through the use of dimethyl terephthalate, dimethyl isophthalate, or dimethyl phthalate in the initial condensation reaction, which are inexpensive chemicals used on a large scale in the polymer industry.

EXPERIMENTAL

General Remarks

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Varian Mercury Plus 400 instrument. Gel permeation chromatography (GPC) results were collected in THF at 40 °C using a Waters Millennium apparatus with polystyrene (PS) standards. The melting (T_m) and glass transition (T_g) temperature data were determined by differential scanning

Table I. Results for the Preparation of High-Molecular Weight Poly(1,4-butylene carbonate-*co*-terephthalate)s and Their Chopping with Polyols^a

Entry	Dimethyl terephthalate (mol % per BD)	Chopper	Yield ^b [g, (%)]	M_n (M_w/M_n) ^c before chopping (kDa)	M_n (M_w/M_n) ^c after chopping (Da)	T_g (°C)	Status [T_m (°C) for wax]
1	30	BD	18.9 [89]	80.9 (1.57)	2200 (1.69)	-42	Wax (43)
2	30	1	19.2 [91]	118 (1.41)	2100 (2.16)	-35	Wax (43)
3	30	2	19.1 [90]	81.7 (1.53)	2000 (2.43)	-28	Wax (44)
4	30	3	19.1 [90]	82.5 (1.44)	1600 (2.04)	-25	Wax (44)
5	10	1	17.0 [90]	72.9 (1.38)	2000 (2.18)	-44	Turbid oil
6	20	1	17.9 [89]	73.5 (1.39)	2100 (2.25)	-39	Wax (50)
7	40	1	19.3 [85]	80.8 (1.49)	2200 (2.17)	-33	Wax (44)
8	50	1	20.7 [87]	78.6 (1.44)	2000 (2.54)	-33	Wax (44)

^aPolymerization conditions: BD (10.0 g, 111 mmol), NaH (0.111 mmol), DMC (DMC) = $1.57 \times$ [(BD) - (dimethyl terephthalate)] in a bath of 120 °C for 1.0 h, while removing methanol at atmospheric pressure (1st step); then at 190 °C successively under 570 mmHg for 0.50 h, 380 mmHg for 1.0 h, 190 mmHg for 2.0 h, and finally at 210 °C under 0.3 mmHg for 2 h (2nd step); addition of chopper (16.7 mmol, 15.0 mol %) followed by stirring for 3 h at 210 - 150 °C.

^b[Mass of the generated polymer]/[theoretically expected mass].

^cMeasured by GPC at 40 °C using PS standards.

reaction pot was fully evacuated (0.3 mmHg) for 2 h at 210 °C. Applying this procedure and conditions, high-molecular weight poly(1,4-butylene carbonate-*co*-terephthalate)s (M_n , 73–120 kDa) were successfully prepared with various [dimethyl terephthalate]/[BD] feed ratios (Table I). As a portion of the feed BD evaporated during the polycondensation reaction, the yield of polymer isolated was approximately 90% and the terephthalate fraction in the resulting polymer was deviated slightly from the [dimethyl terephthalate]/[BD] feed ratio. When applying the same conditions and procedures in the presence of dimethyl isophthalate, high-molecular weight poly(1,4-butylene carbonate-*co*-isophthalate)s were also successfully synthesized with M_n of ~80 kDa (Table II). In the case of dimethyl phthalate, however, low-molecular weight polymers were generated (M_n , 48–83 kDa) (Table III).

Chopping the High-Molecular Weight Poly(1,4-butylene carbonate-*co*-aromatic ester)

During the course of the polycondensation reactions, the viscosity of the mixture increased gradually and the mixture became almost unstirrable by the end of reaction. The addition of chopper, such as diol (BD) or polyol including glycerol propoxylate, 1,1,1-*tris*(hydroxyl)ethane, or pentaerythritol (1–3 in Chart 1), converted, within 10 min, the thick viscous polymer melt to an oily state that could be stirred. Sodium alkoxide (0.1 mol % per BD), which was fed as a catalyst in the polycondensation reaction, also acted as a catalyst in the subsequent chopping process (Scheme 2). When sodium alkoxide catalyst was removed after the polycondensation reaction, the thick polymer melt was not converted to an oily state, indicating sodium alkoxide catalyst is essential in the chopping process. Rapid base-catalyzed

Table II. Results for Preparation of High-Molecular Weight Poly(1,4-butylene carbonate-*co*-isophthalate)s and Their Chopping with Polyols^a

Entry	Dimethyl terephthalate (mol % per BD)	Chopper	Yield ^b [g (%)]	M_n (M_w/M_n) ^c before chopping (kDa)	M_n (M_w/M_n) ^c after chopping (Da)	T_g (°C)	Status [T_m (°C) for wax]	Viscosity (cP)
1	30	BD	18.9 [89]	69.7 (1.50)	2100 (1.62)	-36	Wax (57)	
2	30	1	18.6 [87]	68.0 (1.50)	2200 (2.14)	-35	Clear oil	42,400
3	30	2	18.9 [89]	107 (1.47)	1700 (2.83)	-28	Clear oil	162,000
4	30	3	18.7 [88]	94.4 (1.39)	2000 (1.94)	-24	Turbid oil	
5	10	1	16.7 [88]	72.0 (1.42)	2100 (2.09)	-43	Turbid oil	
6	20	1	17.6 [87]	78.0 (1.56)	2100 (2.20)	-38	Clear oil	101,000
7	40	1	20.2 [90]	82.6 (1.58)	2100 (2.28)	-29	Turbid oil	
8	50	1	21.4 [91]	75.2 (1.56)	2200 (2.19)	-28	Wax (63)	

^aPolymerization conditions: BD (10.0 g, 111 mmol), NaH (0.111 mmol), DMC (DMC) = $1.57 \times$ [(BD) - (dimethyl isophthalate)] in a bath of 120 °C for 1.0 h, while removing methanol at atmospheric pressure (1st step); then at 190 °C successively under 570 mmHg for 0.50 h, 380 mmHg for 1.0 h, 190 mmHg for 2.0 h, and finally at 210 °C under 0.3 mmHg for 2 h (2nd step); addition of chopper (16.7 mmol, 15.0 mol %) followed by stirring for 3 h at 210 - 150 °C.

^b[Mass of the generated polymer]/[theoretically expected mass].

^cMeasured by GPC at 40 °C using PS standards.

Table III. Results for Preparation of High-Molecular Weight Poly(1,4-butylene carbonate-co-phthalate)s and Their Chopping with Polyols^a

Entry	Dimethyl phthalate (mol % per BD)	Chopper	Yield ^b [g (%)]	M_n (M_w/M_n) ^c before chopping (kDa)	M_n (M_w/M_n) ^c after chopping (Da)	T_g (°C)	Status [T_m (°C) for wax]	Viscosity (cP)
1	30	BD	19.2 [91]	58.6 (1.52)	2100 (1.72)	-43	Turbid oil	
2	30	1	18.9 [89]	62.3 (1.49)	2100 (1.85)	-35	Clear oil	67,600
3	30	2	18.3 [85]	71.1 (1.56)	2100 (1.92)	-29	Clear oil	37,500
4	30	3	18.7 [88]	76.4 (1.63)	1600 (1.91)	-24	Clear oil	138,000
5	10	1	16.6 [87]	83.0 (1.61)	1700 (2.12)	-41	Turbid oil	
6	20	1	17.6 [87]	47.8 (1.60)	1900 (2.04)	-36	Clear oil	63,400
7	40	1	20.7 [93]	50.1 (1.74)	1700 (1.99)	-33	Turbid oil	

^aPolymerization conditions: BD (10.0 g, 111 mmol), NaH (0.111 mmol), DMC (DMC) = $1.57 \times [(BD) - (\text{dimethyl phthalate})]$ in a bath of 120 °C for 1.0 h, while removing methanol at atmospheric pressure (1st step); then at 190 °C successively under 570 mmHg for 0.50 h, 380 mmHg for 1.0 h, 190 mmHg for 2.0 h, and finally at 210 °C under 0.3 mm Hg for 2 h (2nd step); addition of chopper (16.7 mmol, 15.0 mol %) followed by stirring for 3 h at 210–150 °C.

^b[Mass of the generated polymer]/[theoretically expected mass].

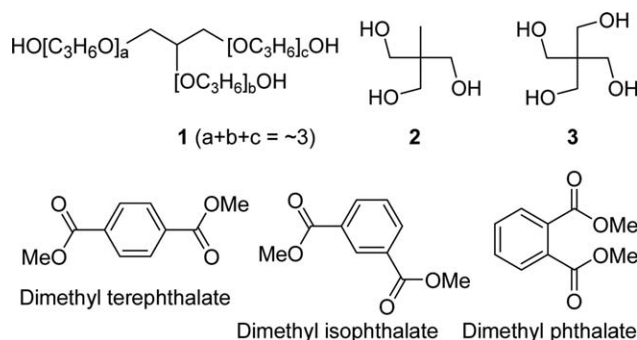
^cMeasured by GPC at 40 °C using PS standards.

transesterification occurred between the —OH groups of the chopper, and the carbonate or ester bonds of the high-molecular weight poly(carbonate-co-aromatic ester). The result of this transesterification process was the formation of macropolyols bearing —OH groups at all chain ends. Since the molecular weights of the generated poly(carbonate-co-aromatic ester)s were sufficiently high, the contribution to the formed macropolyols of the —OMe end groups that the high-molecular weight polymer chains might bear could be ignored, and the molecular weight was theoretically determined by the equation: $M_n = [\text{mass of the generated oil (g)}]/(\text{number of mol of chopper})$.

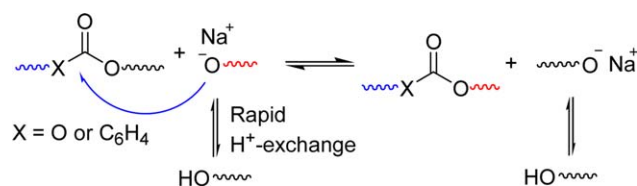
The GPC-measured number average molecular weights (M_n) of the generated oils were in the range of 1600–2200 Da [Tables (I–III)], dramatically lower than the M_n values (50–120 kDa) before chopping (Figure 1). The theoretical molecular weights calculated by the equation $M_n = [\text{mass of the generated oil (g)}]/(\text{number of mol of chopper})$ were in the range of 1000–1400 Da, roughly in agreement with the GPC determined values. The molecular weight distribution values (M_w/M_n) were marginally changed in the cases of chopping with BD [entry 1 in Tables (I–III)], but the M_w/M_n values were higher (1.9–2.5) in the cases where chopping with triols (**1** and **2**) or tetraol (**3**) were performed. The generation of the branched chains in these

cases could have resulted in the broadening of the molecular weight distributions observed. The results were reproducibly obtained when the procedure was repeated (entry 2 in Table II), whereby the M_n (M_w/M_n) values after chopping were consistent [2200 (2.14), 1900 (2.34), and 2000 (2.12) Da], even though the M_n (M_w/M_n) values before chopping varied depending on the extent of polycondensation [68.0 (1.50), 73.1 (1.81), and 77.9 (1.61) kDa].

Chopping of the high-molecular weight chains with a diol (HOAOH, BD in this study) generated macrodiols, whereas chopping with triols [A(OH)₃, **1** and **2**] resulted in the formation of more complicated chain structures (Scheme 3). Macrotriole or macropentaol could be additionally generated if the polymer chain contained one or two triol (A) units, respectively. If an equilibrium state was reached during the transesterification process, a statistical distribution of the 1,4-butylene (—CH₂CH₂CH₂CH₂—) and chopper (A) units in the formed macropolyols can be assumed. The statistics allow for calculation of the mole fraction for each chain bearing k chopper (A) units, f_k [i.e., $x_k/\Sigma(x_k)$, where x_k is the number of moles of each chain], and therefore, $f_0 = {}_aC_0(1-p)^{a-0}(p)^0$, $f_1 = {}_aC_1(1-p)^{a-1}(p)^1$, $f_2 = {}_aC_2(1-p)^{a-2}(p)^2$, $f_3 = {}_aC_3(1-p)^{a-3}(p)^3$, etc. In these equations, ' p ' is $Z/(N+Z)$, where Z is number of moles of chopper (A) units and N is the number of moles of 1,4-butylene units, and ' a ' is the average degree of polymerization, i.e., average repeat (sum of A and 1,4-butylene) units per chain. The value of ' a ' is an integer roughly equal to $(N+Z)/Z$ (i.e., $1/p$), i.e., the total number of repeat units (sum of A



Cha 1. Polyols (1–3) used as choppers and the aromatic esters used in the polycondensation reactions.



Scheme 2. Chopping process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

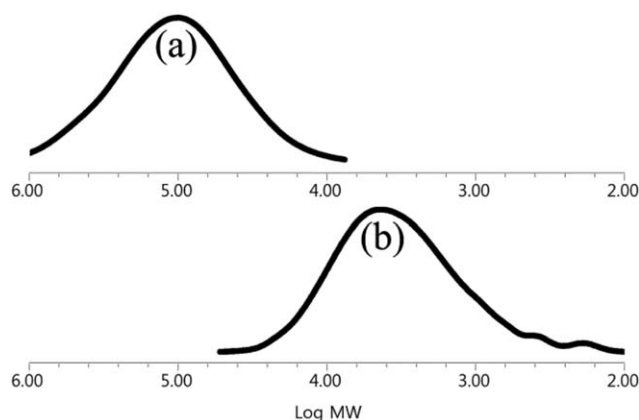


Figure 1. GPC curves (a) before and (b) after chopping.

and 1,4-butylene units) divided by the total number of chains (Z). In our typical experiments, the number of moles of 1,4-butylene units and the number of moles of chopper units were ~ 100 mmol [111 mmol (feed BD) $\times 0.90$ (yield)] and 16.7 mmol, respectively, and the fractions f_0 (macrodiol), f_1 (macrotriol), f_2 (macrotetraol), f_3 , and f_4 (macropentaol) were calculated to be 35, 40, 19, 5.3, and 0.9%, respectively.

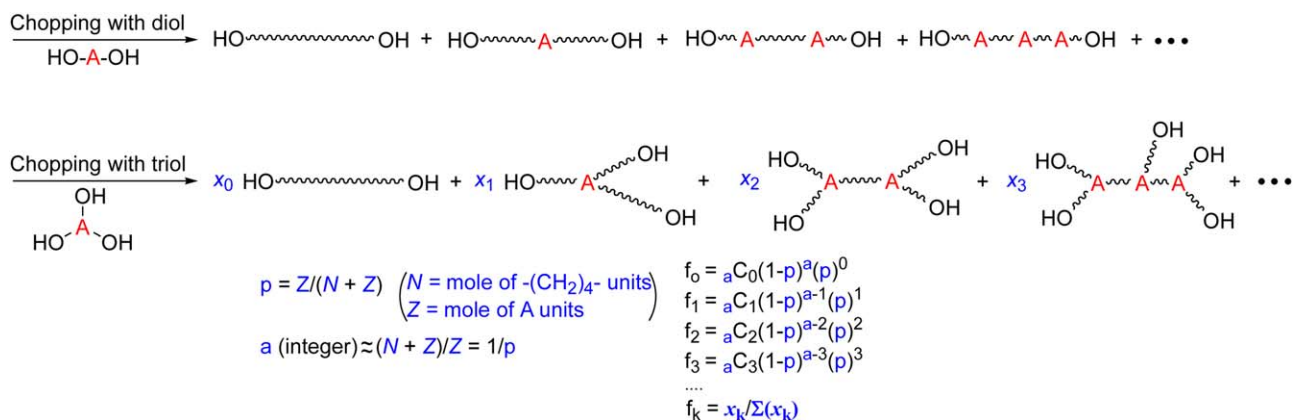
Aliphatic polycarbonate macropolyols are conventionally prepared directly through the polycondensation of a diol or polyol with DMC. The $-\text{OMe}$ groups, which originate from DMC, must be completely removed to prepare macropolyols suitable for use in PU synthesis. In the transesterification (or polycondensation) process, the $-\text{OMe}$ end groups were removed upon formation of the methanol byproduct, which must be immediately and completely excluded from the reaction mixture. Controlling the molecular weight is another important issue in the synthesis of macropolyols. Typically, molecular weight is controlled by the feed ratio of the two components, but DMC is volatile and forms an azeotrope with distilled methanol, making it difficult to control the molecular weight. During the course of complete removal of the $-\text{OMe}$ end groups, an undesirable condensation occurs, resulting in formation of BD, which is also volatile at high temperatures under vacuum. This undesirable reaction results in an increase in the molecular weight of the macropolyols above the desired value. Thus, the chopping

method described in this work may be advantageous over the conventional direct polycondensation method. In fact, preparation of the corresponding macropolyols by the conventional direct polycondensation was unsuccessful in our attempts, as it was difficult to stop the polycondensation process at the appropriate point, yielding higher molecular weight polymers than was desired.

Properties and Characterization of the Macropolyols

Macropolyols, in their oil form, with an appropriate viscosity, are desirable for use in the PU industry. Since poly(1,4-butylene carbonate)-based macrodiols are crystalline, 1,4-butanediol is fed with other diols to inhibit crystallization. Most of the macropolyol samples containing terephthalate units prepared in this work by chopping poly(1,4-butylene carbonate-*co*-terephthalate)s were wax-like materials [Figure 2(a), entries 1–4 in Table I]. A sample prepared by chopping the polymer containing a small amount of terephthalate units (10 mol %) with glycerol propoxylate (**1**) was initially an oily material, but some crystalline particles were generated during its storage, resulting in the initially clear oil becoming turbid [Figure 2(b), entry 5 in Table I]. Macrodiols prepared by chopping poly(1,4-butylene carbonate-*co*-isophthalate) with BD were also wax-like materials (entry 1 in Table II). In contrast, chopping with triol and tetraol (**1–3**) resulted in the formation of oily compounds in most cases (entries 2–7 in Table II); a wax-like material was obtained only when the isophthalate content was high (50 mol %) (entry 8 in Table II). Branched chain topologies typically hampered crystallization, giving viscous oily products.^{37,38} In some cases, storage over several weeks resulted in the formation of small amounts of crystalline materials to turn the clear oils turbid (entries 4, 5, and 7 in Table II), but chopping poly(1,4-butylene carbonate-*co*-isophthalate)s containing 20 and 30 mol % isophthalate units with triols (**1** and **2**) gave persistently clear oily macropolyols (entries 2, 3, and 6 in Table II).

The phthalate units in the macropolyols inhibited the crystallization more efficiently than the terephthalate and isophthalate units. In all cases, oily compounds were generated and, importantly, this clear oily nature was consistently preserved when poly(1,4-butylene carbonate-*co*-phthalate)s containing 20 and 30 mol % phthalate units were chopped with triol or tetraol (**1–3**) [Figure 2(c), entries 2–4 and 6 in Table III]. As a result of



Scheme 3. Chain compositions after chopping. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 2. Status of the macropolymers: (a) wax-like (entry 1 in Table I), (b) turbid oil (entry 5 in Table I), and (c) clear oil (entry 2 in Table III). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the presence of the aromatic ester units, the viscosities of these macropolymers (37,000–138,000 cP) were higher than those of poly(1,4-butylene carbonate)-based macropolymers ($\sim 20,000$ cP) and much higher than those of commercially available macrodiols, e.g., poly(propylene glycol)-diol (1300 cP for M_n 3500 Da), poly(1,6-hexamethylene adipate)-diol (4200 cP at 60 °C for M_n 3800 Da), and poly(1,6-hexamethylene carbonate)-diol (3000–8000 cP at 60 °C for M_n 2000 Da).

The wax-like materials showed melting temperatures (T_m) around 45 °C [close to the T_m of PBC (60 °C)], along with glass transition temperatures (T_g) in the range of -44 to -22 °C in DSC scans [Figure 3(a)], whereas there was no T_m signal for the oily samples [Figure 3(b)]. The T_g of a macropolyol that did not contain aromatic ester units, i.e., a sample prepared by chopping PBC with **1**, was -49 °C.³⁶ By increasing the amounts of terephthalate units to 10, 20, and 30 mol %, the T_g value gradually increased to -44 , -39 , and -35 °C, respectively (entries 5, 6, and 2 in Table I). However, the increase of T_g value was negligible at terephthalate contents above 30 mol %, where T_g was -33 °C for terephthalate contents both of 40 and 50 mol % (entries 7 and 8 in Table I). The T_g value was almost unchanged by variations in the ester units, and the samples prepared by chopping the polymers containing 30 mol % terephthalate, isophthalate, and phthalate units with **1** all showed the same T_g values of -35 °C [entry 2 in Tables (I–III)].

Figure 4 shows a selected region (3.0–5.5 ppm) in the ^1H NMR spectrum of a typical sample prepared by chopping poly(1,4-butylene carbonate-*co*-terephthalate) with glycerol propoxylate (**1**). Broad signals (denoted as 'a') originate from the chopper (glycerol propoxylate). Two triplet resonances at 3.71 and 3.65 ppm (denoted as 'b') can be assigned to the $\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_2\text{OH}$ and $\text{OC}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_2\text{OH}$ end groups, respectively, where it can be seen that the intensity of the former [$\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_2\text{OH}$] increased as the terephthalate content was increased. The resonances at around 4.4 and 4.15 ppm can be assigned to $-\text{C}_6\text{H}_4\text{C}(\text{O})\text{OCH}_2-$ (ester) and $-\text{OC}(\text{O})\text{OCH}_2-$ (carbonate), respectively, with the intensity

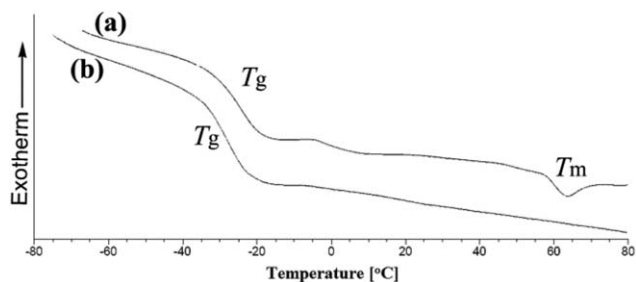


Figure 3. DSC curves: (a) wax-like (entry 8 in Table II) and (b) clear oil (entry 3 in Table II).

of the former [$-\text{C}_6\text{H}_4\text{C}(\text{O})\text{OCH}_2-$] also increasing as the terephthalate content increased. The ester resonance at 4.4 ppm was further split into two resonances at 4.41 (denoted as '1') and 4.36 ppm (denoted as '2'), which are assigned to the BD functionalized with ester groups at both ends [$-\text{C}_6\text{H}_4(\text{CO})\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CO})\text{C}_6\text{H}_4-$], and to BD functionalized with a carbonate group at one end and an ester group at the other [$-\text{O}(\text{CO})\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CO})\text{C}_6\text{H}_4-$], respectively. The carbonate resonance at 4.15 ppm was also split into two resonances at 4.19 ppm (denoted as '3') and 4.14 ppm (denoted as '4'), which are assigned to a BD functionalized with a carbonate group at one end and an ester group at the other [$-\text{O}(\text{CO})\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CO})\text{C}_6\text{H}_4-$], and to BD functionalized with carbonate groups at both ends [$-\text{O}(\text{CO})\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CO})\text{O}-$], respectively. The ratios of the intensities (I) of the four split signals allowed for the calculation of the number-average sequence lengths (L) of butylene terephthalate (BT) and butylene carbonate (BC) units, whereby

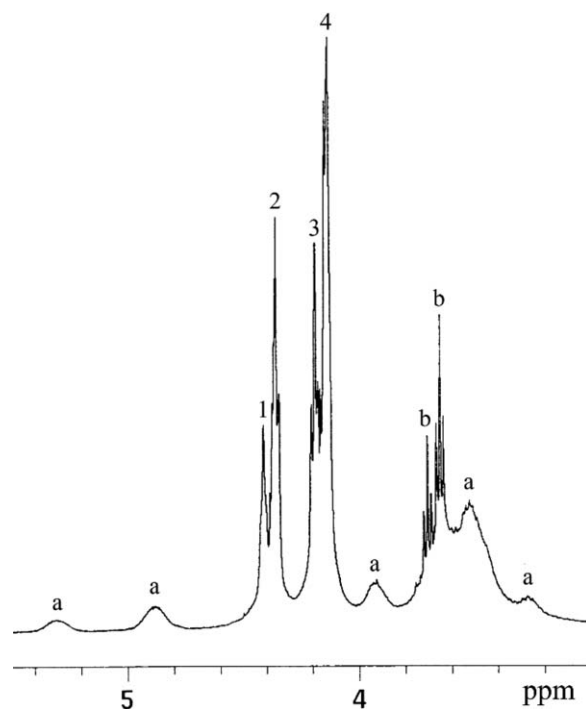


Figure 4. ^1H NMR spectrum of macropolyol prepared by chopping high-molecular weight poly(1,4-butylene carbonate-*co*-terephthalate) with glycerol propoxylate (entry 2 in Table I).

$L_{BC} = (I_4 + I_3)/I_3 = 2.85$ and $L_{BT} = (I_1 + I_2)/I_2 = 1.51$. The degree of randomness (R), calculated from the average sequence lengths ($R = 1/L_{BC} + 1/L_{BT}$) was 1.01, indicating the statistical random distribution of the carbonate and ester units. The R values were calculated to be in the range of 0.98–1.02 for all of the samples containing terephthalate and isophthalate units (Tables I and II), indicating the statistical random distribution of the incorporation of carbonate and ester units to the macropolyol, regardless of changes to the aromatic ester units and choppers used in the synthesis. For the samples containing phthalate units (Table III), neither the ester [$-\text{C}_6\text{H}_4\text{C}(\text{O})\text{OCH}_2-$] nor carbonate ($-\text{OC}(\text{O})\text{OCH}_2-$) signals were split, therefore not allowing for calculation of an R value.

A clear oily compound prepared by chopping a high-molecular weight poly(1,4-butylene carbonate-*co*-isophthalate) with glycerol propoxylate (entry 2 in Table II) was briefly tested in PU synthesis by its reaction with 4,4'-methylene diphenyl diisocyanate in a 1:1 ($-\text{OH}$)/($-\text{NCO}$) ratio using a stannous 2-ethylhexanoate catalyst (0.01 wt % of total solids) according to a previously reported procedure.³⁹ The viscosity of the reaction rapidly increased upon mixing of the two components, and eventually a hard solid was formed by curing at 100 °C for 4 h. This isolated solid was insoluble in any organic solvent, indicating the formation of extensive crosslinking (thermoset).

CONCLUSIONS

High-molecular weight poly(1,4-butylene carbonate-*co*-aromatic ester)s (M_n , 50–120 kDa), with aromatic esters comprised of terephthalate, isophthalate, or phthalate groups, were prepared by the condensation of 1,4-butanediol, dimethyl carbonate, and dimethyl terephthalate (or isophthalate or phthalate) using a sodium alkoxide catalyst. Upon addition of a polyol (1,4-butanediol, glycerol propoxylate, 1,1,1-*tris*(hydroxymethyl)ethane, or pentaerythritol), the high-molecular weight polymers were degraded or chopped into low-molecular weight macropolyols of 2000–3000 Da (M_n). The majority of the samples containing terephthalate units were wax-like materials with melting temperatures around 45 °C, whereas those containing isophthalate and phthalate units showed the propensity to be oily. The glass transition temperatures of the macropolyols gradually increased from -50 to -30 °C upon increases in the amount of the aromatic ester units incorporated into the macropolyols up to 30 mol %, but above 30 mol %, this temperature remained constant at around -30 °C. The viscosities of the macropolyols were higher when ester units were incorporated in the molecule. The chopping method developed in this study may be advantageous in the synthesis of aliphatic polycarbonate-based macropolyols over the conventional direct condensation method, as the molecular weight can be more readily controlled and the chain compositions more easily estimated. The materials prepared in this work are new compounds prepared using benign dimethyl carbonate, which is currently produced on a large scale from CO_2 and the abundant dimethyl terephthalate (or isophthalate or phthalate), and may have the potential to be used in the polyurethane industry.

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