

# Synthesis of Functionalizable and Biodegradable Polymers via Ring-Opening Polymerization of 5-Benzyloxy-Trimethylene Carbonate and $\epsilon$ -Caprolactone

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Received 10 December 2010; accepted 21 April 2011

DOI 10.1002/app.34735

Published online 23 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The biomedical applications of poly( $\epsilon$ -caprolactone) (PCL) were limited for its high hydrophobicity and crystallinity. In this study, we copolymerized CL with amorphous 5-hydroxyl-trimethylene carbonate (HTMC) to solve the problem. The 5-benzyloxy-trimethylene carbonate (BTMC) was synthesized to copolymerize with CL, then hydrogenolyzed to obtain hydroxyl pendant groups. A series of copolymers with different BTMC molar ratio were synthesized and their chemical structures and thermal properties were thoroughly studied with NMR, FT-IR, GPC, XRD, DSC, and TGA. Finally we examined the water contact angle of the copolymers. DSC and XRD results

showed that the PCL segments in the copolymers crystallized below 16.8%. BTMC molar content and the crystallinity of the copolymers increased after hydrolysis. With the introduced hydroxyl pendant groups, the deprotected copolymers improved their hydrophilic property significantly, and the copolymer with 9.3% HTMC molar content had static water contact angle as low as 36.5°. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2204–2210, 2012

**Key words:** functionalization of polymers; hydrophilic polymers; poly(5-hydroxyl-trimethylene carbonate-co- $\epsilon$ -caprolactone); polycarbonates

## INTRODUCTION

As a biodegradable and bioabsorbable polymer, poly( $\epsilon$ -caprolactone) (PCL) has been widely used in biomedical engineering for its excellent mechanical properties, good biocompatibility, low toxicity, and nonimmunogenicity.<sup>1,2</sup> But the high crystallinity and hydrophobicity of PCL, which lead to long degradation, limit its usage in tissue engineering applications.<sup>2–4</sup>

Many strategies have been carried out to solve the above problems. By introducing hydrophilic poly(ethylene glycol) (PEG) segments, PEG-PCL block copolymers had much better hydrophilicity compared with PCL.<sup>5</sup> However, these copolymers had

poor mechanical strength and poor cell affinity, because the PEG segments decreased their molecular weight and had intrinsic anticell adhesion property.<sup>6</sup> Another paper reported that copolymerization of CL and lactones such as lactide and glycolide could decrease the crystallinity, but polylactide and polyglycolide were hydrophobic biodegradable polymers and contributed little to improve the hydrophilicity.<sup>7</sup> Recently, the copolymerization of CL and malolactone was reported to endue the copolymers with functionalizable carboxyl pendant groups<sup>8</sup> to enhance the hydrophilicity and flexibility of the copolymers, but the molecular weights of the copolymers were too low to be used in tissue engineering. Another problem faced was that the strong acidity of malic acid was demonstrated to affect the cell adhesion, change the environmental pH value, and aggravate the local inflammation *in vivo* applications.<sup>9,10</sup>

Aliphatic polycarbonates are amorphous, elastic, and biodegradable polymers, preferable for the modification of aliphatic polyesters to increase flexibility and avoid acidity.<sup>11,12</sup> The aliphatic polycarbonates were usually synthesized by the ring-opening polymerization of trimethylene carbonate (TMC) and its derivatives.<sup>13</sup> 5-Benzyloxy-trimethylene carbonate (BTMC) is a carbonate monomer with pendant group.<sup>11</sup> The copolymers of BTMC and lactones

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Contract grant sponsor: National Basic Research Program of China; contract grant number: 2005 CB623903.

Contract grant sponsor: National Science Foundation of China; contract grant numbers: 20604016, 50830105.

Contract grant sponsor: Sichuan Youth Science and Technology Foundation; contract grant number: 07ZQ026-013.

Contract grant sponsor: Key Project of Chinese Ministry of Education; contract grant number: 109133.

could be functionalized with hydroxyl pendant groups to increase hydrophilicity. The copolymerizations of BTMC with lactones such as 1,4-dioxan-2-one,<sup>14</sup> glycolide,<sup>15</sup> lactide,<sup>16</sup> and other carbonates monomers<sup>17,18</sup> were intensively studied. Recently, a communication reported the copolymer of BTMC and CL with low molecular weight, so the copolymer was only fabricated into nanoparticles for drug delivery.<sup>19</sup> After removing the benzyl groups, the PHTMC degraded almost thoroughly in only 14 days *in vitro*, which showed the functional polycarbonate to be a biodegradable biomaterial.<sup>20</sup>

In this article, we synthesized functionalizable and biodegradable poly(5-benzoyloxy-trimethylene carbonate-*co*- $\epsilon$ -caprolactone) (PBTMCCL) and poly(5-hydroxyl-trimethylene carbonate-*co*- $\epsilon$ -caprolactone) (PHTMCCL) with high molecular weight. Then their chemical structure and thermal properties were studied thoroughly. The copolymerization of BTMC and CL was carried out in the presence of stannous octanoate as catalyst and hydrogenolyzed to obtain PHTMCCL. Both polymers were measured with <sup>1</sup>H NMR, FT-IR, and GPC to characterize their structure and molecular weight. Their thermal properties and crystallinity were studied with DSC, TGA, and XRD. Finally, the water contact angle of the copolymers was measured to characterize their hydrophobicity and hydrophilicity.

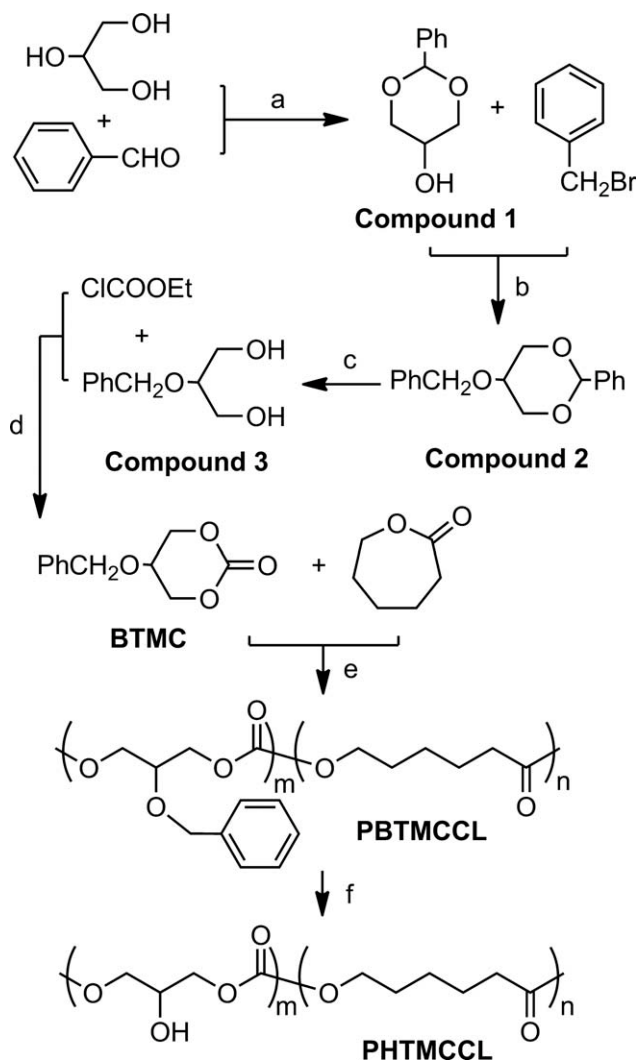
## EXPERIMENTAL

### Materials

Stannous octanoate ( $\text{Sn}(\text{Oct})_2$ ) was purchased from Aldrich and used as received.  $\epsilon$ -Caprolactone was purchased from Aldrich and dried by calcium hydride ( $\text{CaH}_2$ ) before used. Other chemicals were purchased from Ke-Long Chemical (Chengdu, China). Tetrahydrofuran (THF) and ethyl ether were dried with sodium and distilled. Triethylamine, dimethylformamide (DMF), benzaldehyde, ethyl chloroformate, ethanol, and glycerol were analytical pure reagents and purified with general methods. Benzyl bromide (BnBr) and sodium hydride (NaH) were analytical pure reagents and used as received.

### Measurements

<sup>1</sup>H NMR spectra were recorded on Bruker Avance II NMR Spectrometer working at 400 MHz at room temperature (RT). Chloroform-*d* ( $\text{CDCl}_3$ ) or DMSO-*d*<sub>6</sub> was used as solvent with tetramethylsilane (TMS) as internal standard. FT-IR spectra were recorded on Perkin-Elmer Spectrum One FT-IR Spectrometer over the wave number range 400–4000  $\text{cm}^{-1}$ . XRD (X' Pert Pro MPD, Philips, Netherlands) was employed to study the crystalline property of sam-



**Scheme 1** The synthetic pathway for glycerol-based polycarbonates: (a) benzaldehyde/concentrated sulfuric acid, room temperature; (b) NaH/DMF/Benzyl bromide, 0°C and room temperature; (c)  $\text{CH}_3\text{OH}/\text{HCl}$  (aq), reflux; (d) ethyl chloroformate/triethylamine/THF, 0°C and room temperature; (e) bulk polymerization,  $\text{Sn}(\text{Oct})_2$ , 150°C; (f)  $\text{H}_2/\text{Pd}/\text{C}$  (10%), solvent: DMF/ $\text{CH}_3\text{OH}$  (5:1), room temperature.

ples with angle ranging from 5° to 45°. TA DSC Q2000 differential scanning calorimeter was used to carry DSC measurements. The molecular weight ( $M_n$  and  $M_w$ ) and the molecular weight distribution (MWD) were determined by GPC (Waters 1515 Isocratic HPLC Pump and 2414 Refractive Index Detector) with respect to polystyrene standards, at 25°C with tetrahydrofuran as eluent at a flow rate of 1.0  $\text{mL min}^{-1}$ . TGA measurement was made using Netzsch STA499C thermal analyzer with  $\text{Al}_2\text{O}_3$  crucible. The mass loss of the samples was monitored from room temperature to 600°C at a heating rate of 10°C  $\text{min}^{-1}$  in a dynamic nitrogen atmosphere. The water contact angles were recorded on Kruss DSA100 Contact Angle Goniometer Protocol.

**TABLE I**  
The Compositions and Molecular Weights of PCL, PBTMCCL, and PBTMC

Entry <sup>b</sup>	BTMC (mol %)		Molecular weight <sup>a</sup> ( $\times 10^4$ )			Yield (%)
	Feeding	Polymer <sup>c</sup>	$M_n$	$M_w$	$M_w/M_n$	
PCL A		0	–	–	–	97.30
PBTMCCL B	5	4.2	16.05	17.89	1.11	91.85
PBTMCCL C	10	9.3	10.19	13.34	1.31	95.74
PBTMCCL D	20	16.8	7.84	10.87	1.39	90.53
PBTMCCL E	40	34.2	6.98	9.99	1.43	90.63
PBTMCCL F	70	66.1	4.23	6.28	1.49	94.31
PBTMC G		100	7.19	10.26	1.43	90.56

<sup>a</sup> GPC results.

<sup>b</sup> Catalyst octanoate (1% molar ratio of monomers).

<sup>c</sup> Calculated from <sup>1</sup>H NMR.

## Synthesis

### Synthesis of BTMC

The following procedure was changed from the published method.<sup>10,21,22</sup> Benzaldehyde (53 g, 0.5 mol), glycerol (46 g, 0.5 mol) and concentrated sulfuric acid (0.05 mL) were mixed together and stirred vigorously at room temperature for 4 h in nitrogen atmosphere. The mixture was heated to 40°C under reduced pressure to remove the water formed during the condensation reaction and stirred for another 1 h at room temperature. After ethyl ether (75 mL) was added, the mixture was washed with 10% Na<sub>2</sub>CO<sub>3</sub> (aq) and saturated NaCl (aq) till pH = 7.0. The organic layer was dried over anhydrous magnesium sulfate overnight. After filtered, the mixture was crystallized at –20°C to produce crude product 5-hydroxy-1,3-benzylidenglycerol (compound **1** in Scheme 1, yield: 40%).

Under nitrogen atmosphere, compound **1** (20 g, 110 mmol) in DMF (300 mL) was dripped into NaH (5.2 g, 221 mmol) at 0°C and the mixture was stirred for 2 h. Then BnBr (33 mL, 277 mmol) was added at 0°C and stirred for 48 h at room temperature. Having removed DMF, the product was dissolved in CHCl<sub>3</sub> and washed with saturated NaCl (aq) for several times. The organic layer was dried over anhydrous magnesium sulfate and evaporated to get crude product, which was crystallized twice in ethanol at 4°C to obtain pure 5-benzyloxy-1,3-benzylidenglycerol (compound **2** in Scheme 1, yield: 50%).

The 5-benzyloxy-1,3-benzylidenglycerol (10 g, 37 mmol) was dissolved in a mixture solvent of 1M HCl (aq) (40 mL) and CH<sub>3</sub>OH (40 mL) and refluxed for 2 h. After adjusted to pH = 7, the solution was concentrated and extracted with ethyl acetate. The organic layer was dried by anhydrous magnesium sulfate overnight and evaporated to produce 2-benzyloxy-1,3-propanediol (compound **3** in Scheme 1, yield: 95%).

The 2-benzyloxy-1,3-propanediol (10 g, 55 mmol) was stirred with ethyl chloroformate (13.3 g, 120 mmol) in THF (200 mL). Triethylamine (12.4 g, 124 mmol) was added dropwise into the mixture at 0°C and stirred for 2 h at room temperature. After filtered, the solvent was evaporated and the crude product was crystallized in ethyl acetate at –20°C for several times to obtain pure BTMC (yield: 40%).

### Copolymerization of BTMC and CL

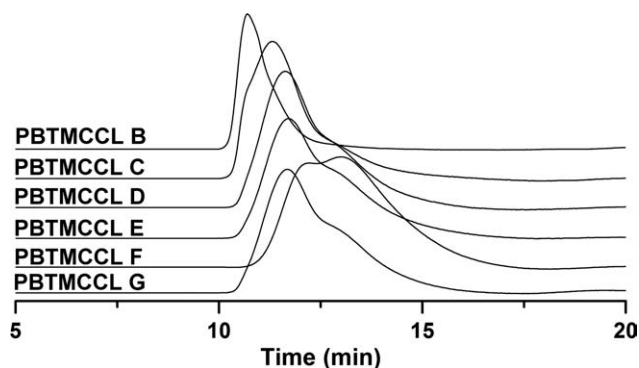
Prescribed amount of BTMC and CL with different molar ratios and catalyst stannous octanoate (1% molar ratio of monomers) (Table I) were put into 5 mL polymerization tubes with oval bottoms and thin and long bottlenecks. After purged with nitrogen and degassed, the tubes were sealed at the bottlenecks under vacuum and placed in oil bath at 150°C for 48 h. Finally different polymers were dissolved in CHCl<sub>3</sub> and precipitated in CH<sub>3</sub>OH to obtain PCL, PBTMCCL with different BTMC molar ratios and PBTMC. The polymers were dried under vacuum at room temperature for 4 days.

### Hydrogenolysis of PBTMCCL

PBTMCCL (0.3 g) and 10% Pd/C (100 mg) in the solution of DMF (25 mL) and CH<sub>3</sub>OH (5 mL) was bubbled with dry H<sub>2</sub> in the water-free system and agitated continuously for 72 h at room temperature. After filtered and concentrated, the mixture was precipitated in ethyl ether to obtain the PHTMCCL, which was dried under vacuum at room temperature for 3 days.

## RESULTS AND DISCUSSION

The synthetic route was shown in Scheme 1. Sn(Oct)<sub>2</sub> was chosen because it catalyzed the ring-opening polymerization of BTMC and CL effectively. The compositions and molecular weights of the

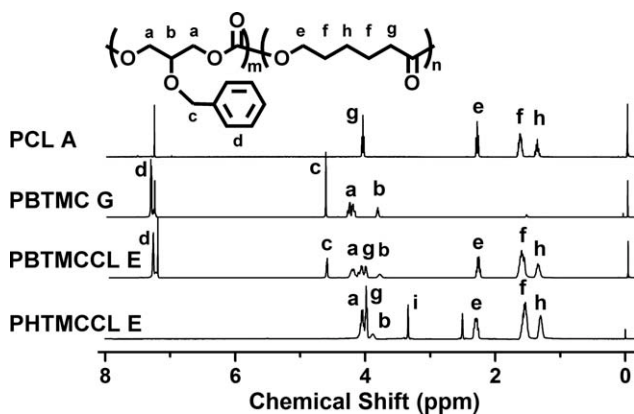


**Figure 1** The GPC spectra of PBTMCCL B(4.2%), C(9.3%), D(16.8%), E(34.2%), F(66.1%), and PBTMC G.

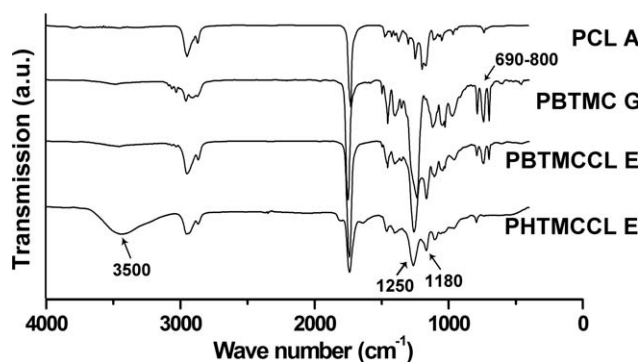
PBTMCCL copolymers were shown in Table I. The molar ratios of BTMC in the copolymers were lower than those in the corresponding feeding doses and the average molecular weight ( $M_w$ ) decreased as BTMC content increased, which indicated that CL was more reactive than BTMC in the copolymerization due to the stereo hindrance effect of the benzyl groups.<sup>23</sup> However as to PBTMCCL E (34.2%) and F (66.1%), CL would insert into the main chain of PBTMC randomly and break the ordered structure of PBTMC, which resulting the decreased  $M_w$  compared with PBTMC.

### GPC measurement

The GPC spectra of the PBTMCCL copolymers were shown in Figure 1. The peaks in the curves were more like a Gauss distribution in the spectra of PBTMCCL B (4.2%) and C (9.3%). A shoulder peak in low molecular portion appeared at PBTMCCL D (16.8%), which became stronger while BTMC molar content increased, even almost splitting into two peaks at PBTMCCL F (66.1%) due to the different activities of the two monomers. In the spectrum of



**Figure 2** The chemical structure of PBTMCCL and the  $^1\text{H}$  NMR spectra of PCL A, PBTMC G, PBTMCCL E(34.2%),  $\text{CDCl}_3$  as solvent; PHTMCCL E(34.2%),  $\text{DMSO-}d_6$  as solvent. All data was acquired at room temperature.



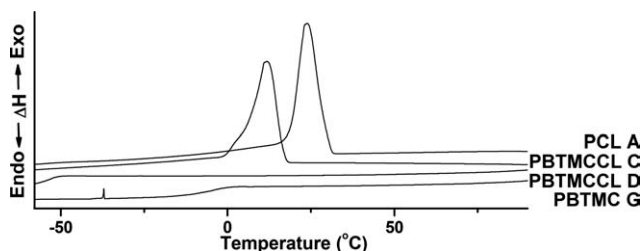
**Figure 3** The FTIR spectra of PCL A, PBTMCCL/ PHTMCCL E(34.2%) and PBTMC G.

PBTMC G, the shoulder peak also existed but it was very weak.

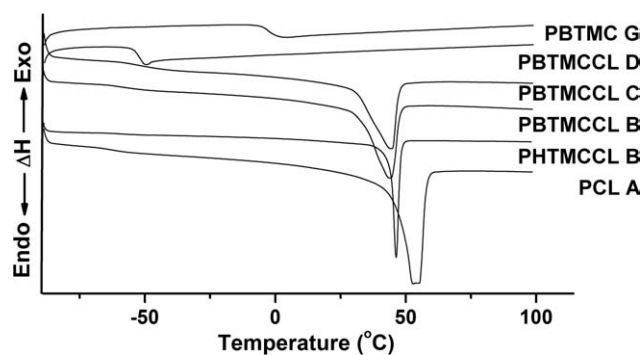
### NMR measurement

Figure 2 showed the  $^1\text{H}$  NMR spectra of PCL A, PBTMC G, PBTMCCL E (34.2%), and PHTMCCL E (34.2%). There were four protons with different chemical environments in the spectrum of PBTMC: 7.3 (m, 5H,  $\text{C}_6\text{H}_5$ ), 4.6 (m, 2H,  $\text{OCH}_2\text{Ph}$ ), 4.2 (m, 4H,  $\text{OCH}_2$ ), 3.8 (m, 1H,  $\text{OCH}$ ). There were only four proton signals in the spectrum of PCL because  $\text{COCH}_2\text{CH}_2\text{CH}_2$  and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  contributed to the same signal peak at  $\delta = 1.6$  ppm (f) for their similar chemical environment and the other three protons of  $\text{COCH}_2$  (g),  $\text{CH}_2\text{CH}_2\text{CH}_2$  (h), and  $\text{CH}_2\text{CH}_2\text{O}$  (e) produced the signals at  $\delta = 4.0$ , 1.4, and 2.3 ppm, respectively. In the spectrum of PBTMCCL E (34.2%), the signals both in CL and BTMC units all located nearly at the same sites as those in the spectra of PCL A and PBTMC G. The integrity of the peaks of  $\text{CH}_2\text{C}_6\text{H}_5$  in BTMC units at  $\delta = 4.6$  ppm and  $\text{OCH}_2$  in CL units at  $\delta = 2.3$  ppm were employed to calculate the compositions of the copolymers.

The PBTMCCL copolymers and PBTMC G were hydrogenolyzed in the presence of Pd/C under hydrogen atmosphere to obtain PHTMCCL and PHTMC G. In the  $^1\text{H}$  NMR spectrum of PHTMCCL E (34.2%), all the protons were around those in PBTMCCL E (34.2%) and the integrity ratios were



**Figure 4** The DSC spectra of PCL A, PBTMCCL C(9.3%)/ D(16.8%) and PBTMC G in the cooling process.



**Figure 5** The DSC spectra of PCL A, PBTMCCL B(4.2%)/C(9.3%)/D(16.8%), PHTMCCL B(4.2%), and PBTMC G in the heating process.

nearly the same. The two protons signals of  $\text{OCH}_2\text{C}_6\text{H}_5$  at  $\delta = 7.3$  and  $4.6$  ppm in the pendant benzyloxy groups disappeared after hydrogenolysis, and the signal corresponding to  $\text{OH}$ 's proton (i) of PHTMCCL E (34.2%) appeared at  $\delta = 3.3$  ppm.

#### FT-IR measurement

The FT-IR spectra of PCL A, PBTMC G, PBTMCCL E (34.2%) and PHTMCCL E (34.2%) were presented in Figure 3. The main variations of the absorbance were in the fingerprint area at around  $1250$ ,  $1180$ , and  $690\text{--}800\text{ cm}^{-1}$ . When the content of PBTMC segments increased, the vibration of the ether bond in PCL segments ( $\text{CO-O-C}$ ) at around  $1180\text{ cm}^{-1}$  decreased while that in carbonate fragments ( $\text{C-O-CO-O-C}$ ) at around  $1250\text{ cm}^{-1}$  and the benzyl groups vibration at  $690\text{--}800\text{ cm}^{-1}$  strengthened, indicating the success of copolymerization of the polymers with different BTMC/CL molar ratio.

Because of the removal of benzyl groups, the characteristic absorbance of substituted benzyl groups at  $698$  and  $741\text{ cm}^{-1}$  weakened or vanished. Meanwhile the absorbance of the hydroxyl groups at around  $3500\text{ cm}^{-1}$  strengthened greatly and increased as HTMC content increased in the PHTMCCL. Both the

$^1\text{H}$  NMR and FT-IR spectra of PHTMCCL implied the success of hydrogenolysis of PBTMCCL.

#### Thermal property characterization

The DSC spectra of the copolymers in cooling and heating processes were presented in Figures 4 and 5, respectively. Four kinds of polymers, PCL A, PBTMCCL C (9.3%)/D (16.8%) and PBTMC G in the cooling process showed the cooling crystalline temperature ( $T_c$ ). The  $T_c$  of the copolymers decreased as the BTMC molar contents increased, even the  $T_c$  could not be observed with the BTMC molar content exceeded 16.8%. The  $T_c$  and  $T_m$  of PCL A, PBTMCCL B (4.2%) and PBTMCCL C (9.3%) decreased gradually and could not be obtained in PBTMCCL D (16.8%)/E (34.2%)/F (66.1%) and PBTMC G for the hindrance of benzyloxy groups in BTMC.  $T_g$  of the polymers continued to increase as BTMC mol % increased for the higher  $T_g$  of PBTMC than that of PCL. The  $T_c$  and  $T_m$  of PCL A, PBTMCCL B (4.2%) and PBTMCCL C (9.3%) decreased gradually and could not be obtained in PBTMCCL D (16.8%)/E (34.2%)/F (66.1%) and PBTMC G while  $T_g$  could always be measured. The range of  $T_m$  of PHTMCCL B (4.2%) was narrower and relatively higher than that of PBTMCCL B (4.2%).

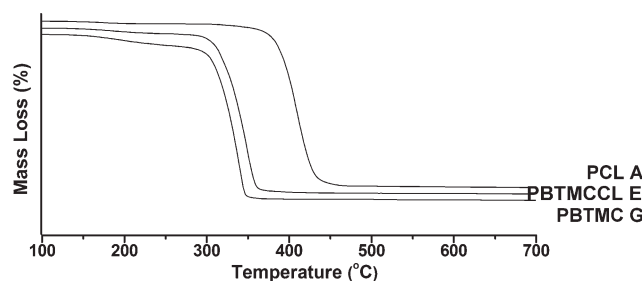
The thermal properties of the copolymers were integrated in Table II, varying regularly with the compositions regard to PBTMCCL. From PCL A to PBTMC G, higher BTMC content led to higher  $T_g$ . After hydrogenolysis, the  $T_g$  of PHTMCCL B (4.2%)/C (9.3%)/D (16.8%)/E (34.2%) was around that of corresponding PBTMCCL, but the  $T_m$  and  $\Delta H$  became higher compared with PBTMCCL while the  $T_c$  on the contrary. Compared with PBTMCCL, the  $T_c$  and  $T_m$  were only detected in PHTMCCL D (16.8%). The above results could be attributed to the large stereo hindrance of the pendant benzyloxy groups in PBTMCCL which blocked its mobility and the  $T_g$  increased with BTMC contents increased. As to

**TABLE II**  
The Integrated Thermal Properties Data of PBTMCCL Copolymers and PHTMCCL Copolymers with Different BTMC/HTMC Molar Ratios: PCL A(0%); PBTMCCL/PHTMCCL: B(4.2%), C(9.3%), D(16.8%), E(34.2%), F(66.1%); PBTMC/PHTMC G(100%)

Entry	$T_g$ ( $^{\circ}\text{C}$ )		$T_c$ ( $^{\circ}\text{C}$ )		$T_m$ ( $^{\circ}\text{C}$ )		$\Delta H$ ( $\text{J g}^{-1}$ )	
PCL A	-70.0		24.3		54.1		33.7	
PBTMCCL/PHTMCCL B	-61.1	-60.0	12.4	11.1	43.7	46.1	27.7	34.3
PBTMCCL/PHTMCCL C	-52.2	-54.6	6.8	1.2	43.6	49.9	21.1	41.3
PBTMCCL/PHTMCCL D	-50.4	-53.2	-	-6.7	-	19.0	-	1.5
PBTMCCL/PHTMCCL E	-34.5	-36.8	-	-	-	-	-	-
PBTMCCL/PHTMCCL F	-13.2	-39.8	-	-	-	-	-	-
PBTMC/PHTMC G	-0.7	-15.1	-	-	-	-	-	-

-: Data not obtained.

Abbreviations:  $T_g$ : glass transition temperature;  $T_c$ : cooling crystalline temperature;  $T_m$ : melting temperature;  $\Delta H$ : enthalpy change.



**Figure 6** The TGA spectra of PCL A, PBTMCCL E(34.2%), and PBTMC G.

PHTMCCL, the hydrogen bonding interactions between the hydroxyl groups after hydrogenolysis led to the same regular variations of  $T_g$ .

The PBTMC or PHTMC segments destroyed the regularity and crystallization of PCL chains, resulting in the lower  $T_m$  of PBTMCCL and PHTMCCL than that of PCL homopolymer and the decrease of the  $\Delta H$  while BTMC contents increased. But the  $\Delta H$  of PHTMC was higher because the hydrogen bonding interaction partially limited the movement of PCL segment, resulting in the higher crystallinity.<sup>7</sup>

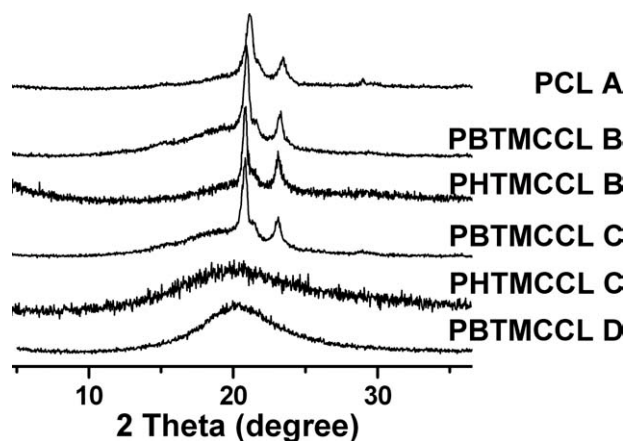
The TGA spectra of PCL (A), PBTMCCL E (34.2%) and PBTMC G were presented in Figure 6 and the data was presented in Table III. The start decomposition temperature was PBTMC < PBTMCCL E (34.2%) < PCL but the decomposition speed was PBTMC > PBTMCCL E (34.2%) > PCL. All samples showed one decomposition step with different temperature ranges that were 310–360 °C of PBTMC and PBTMCCL E (34.2%) and 380–430 °C of PCL.

### XRD measurement

XRD was used to study the crystallization of the polymers. The XRD spectra of different polymers were shown in Figure 7. The PCL A and PBTMCCL B (4.2%) and C (9.3%) showed strong crystalline ability and the crystal peaks appeared at  $2\theta = 21.7^\circ$  and  $24.1^\circ$ , implying that the PCL segments in the copolymers also crystallized, but the PCL crystal could not be observed in the copolymer with above 16.8 mol % BTMC. Besides, crystal peaks disappeared in PHTMCCL C (9.3%) compared to PBTMCCL C (9.3%) due to the hydrogen bonds between the large amounts of hydroxy group in the former. According

**TABLE III**  
The TGA Data of PCL A, PBTMCCL E(34.2%), and PBTMC G

Entry	Onset (°C)	Mid (°C)	Inflection (°C)	End (°C)	Mass loss (%)
PCL A	387.2	408.2	410.8	429.0	93.45
PBTMCCL E	320.3	339.8	348.7	359.5	91.43
PBTMC G	314.5	330.3	339.7	346.6	87.78



**Figure 7** The XRD spectra of PCL A, PBTMCCL B(4.2%)/C(9.3%)/D(16.8%), and PHTMCCL B(4.2%)/C(9.3%).

to the spectra, the crystalline ability of PHTMCCL B (4.2%) was higher than that of PBTMCCL B (4.2%).<sup>24</sup> The XRD results were consistent with the DSC results.

### Water contact angle

Water contact angle is an important parameter to evaluate the hydrophilicity of materials. The PBTMCCL copolymers were functionalized with hydroxyl pendant groups after hydrogenolysis to improve their hydrophilicity. The static water contact angles of the copolymers were tested and integrated in Table IV. The static water contact angle of the polymers increased from  $77.3^\circ$  to  $99.6^\circ$  when the BTMC content in the copolymers increased from 0 to 100 mol %. Because the hydrophobicity of the benzyloxy groups were higher than that of PCL chains, increase of BTMC content would cause the copolymer more hydrophobic, leading to higher static water contact angles.

After hydrogenolysis, the benzyloxy groups were changed to hydrophilic hydroxyl groups and the hydrophilicity of the copolymer increased greatly. The static water contact of PHTMCCL C (9.3%) was as low as  $36.5^\circ$ . But when the HTMC were higher than 9.3 mol %, the water dripped on the polymeric

**TABLE IV**  
The Water Contact Angles of PCL, PBTMC/PHTMC, and PBTMCCL/PHTMCCL with Different BTMC/HTMC Molar Ratios: PCL A(0%); PBTMCCL/PHTMCCL: B(4.2%), C(9.3%), D(16.8%), E(34.2%), F(66.1%); PBTMC/PHTMC G(100%)

Entry	Water contact angle (degree)						
	A	B	C	D	E	F	G
PBTMCCL	77.3	88.6	92.6	94.8	96.1	97.3	99.6
PHTMCCL		62.7	36.5	–	–	–	–

–: Data not obtained.

films spread too fast to be recorded. On the PBTMCCL film surface, the water drops spread slowly and could keep their shapes for several minutes while on PHTMCCL film surface the water drops spread to water films within several seconds.

From the above structure characterizations, we successfully integrated the amorphous carbonate segment into the PCL, which could help to control the degradation of the copolymer and improve its hydrophilicity. Having synthesized a serial of such copolymers and studied their thermal and crystalline properties, we thought PHTMCCL C (9.3%) would be promising for the usage in tissue engineering because of its high molecular weight and suitable  $T_g$  and  $T_m$ . Moreover, the copolymer had good hydrophilic property and the hydroxyl groups of the polymer could be chemically changed to other functional groups to satisfy various usages.

### CONCLUSIONS

The 5-benzyloxy-trimethylene carbonate was copolymerized with  $\epsilon$ -caprolactone and hydrogenolyzed to prepare functionalizable and biodegradable PHTMCCL. The copolymerizations with different BTMC/CL ratios were studied and the proportions of BTMC in the copolymers were lower than those in the feeding doses. With increasing BTMC contents,  $M_w$  of PBTMCCL decreased while  $T_g$  increased. The PCL segments in PBTMCCL crystallized when the BTMC content was lower than 16.8 mol %. Both DSC and XRD results showed that the crystallinity of PHTMCCL were higher than that of the corresponding PBTMCCL. The hydrophilicity of PHTMCCL was greatly improved and the static water contact angle of PHTMCCL C (9.3%) was as low as 36.5°.

Compared among these copolymers synthesized above, we believe that polycarbonate PHTMCCL C (9.3%) with enough molecular weight (1.33E5), suitable hydrophilic (water contact angle 36.5°), func-

tionizable and biodegradable properties has great potential as tissue engineering scaffold materials.

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