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Preparation of block copolymer of ε-caprolactone and 2-methyl-2-carboxyl-propylene carbonate

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Abstract

A block copolymer PCL-*b*-PMBC of ε-caprolactone (ε-CL) and 2-methyl-2-benzyloxycarbonyl-propylene carbonate (MBC) was synthesized by sequential ring-opening polymerization of the ε-CL and MBC monomers with amino isopropoxyl strontium (Sr-PO) as an initiator. It was debenzylated by catalytic hydrogenation to obtain a linear block copolymer PCL-*b*-PMCC with pendant carboxyl groups. WAXD showed that the presence of PMBC segment in PCL-*b*-PMBC influenced obviously the crystallizability of PCL block, in agreement with the DSC results. Diffraction peak of PCL-*b*-PMCC after debenzylation was hardly observed and moreover, melting enthalpy ΔHm of PCL-*b*-PMCC was 10.9 J/g compared to 68.0 J/g of PCL-*b*-PMBC, due to the replacement of the benzyl ester by the carboxyl group. The presence of carboxyl groups is expected to enhance the biodegradability of the copolymer and to facilitate a variety of medical applications.

Keywords: Biodegradable; Block polyesters; Functional polymers

1. Introduction

Poly(ε-caprolactone) (PCL) has received steadily increasing attention for medical applications over the past 20 years, because of its unique properties such as biodegradability, biocompatibility, miscibility with other polymers, permeability to a wide range of drugs, and so forth [1–3]. However, its high hydrophobicity, high crystallinity, slow biodegradation rate and, especially, lack of chemical reactivity have considerably limited its medical applications. Therefore, its modification is necessary. Poly(ethylene oxide-*b*-ε-caprolactone) has attracted much attention, because this kind of polyester-polyether-type block copolymer has a superior amphiphilic property as compared with the parent PCL homopolymer [4–10]. Block copolymer of ε-caprolactone with vinyl pyrrolidone also exhibits amphiphilic property by forming micelles of 30–80 nm [11]. Copolymerization of ε-caprolactone with other cyclic ester monomer [12–17], such as lactide, carbonate et al., improves the crystallinity and biodegradation of PCL. Recently, functionalized cyclic monomers such as NCA's of amino acids [18], (3 s)-[(benzoxylcarbonyl) methyl]-morpholine-2, 5-dione [19] and ε-caprolactones bearing carboxyl [20] or hydroxyl [21] groups have been used as the comonomers to prepare functionalized poly(ε-caprolactone)s. They are expected to have enhanced chemical reactivity and to facilitate further modifications to improve the bio-compatibility and bio-affinity. But some of these monomers are difficult to synthesize such as functionalized ε-caprolactones, some are difficult to copolymerize with ε-caprolactone so that the copolymers with high molecular weights are hardly obtained.

On the other hand, aliphatic polycarbonate is a well-known biodegradable polymer [22–25], and 1, 3-propylene carbonate was found to be polymerized and copolymerized with cyclic ester monomers easily [26,27]. Therefore, we tried to take this advantage to prepare functionalized PCL. The strategy was first to prepare a functionalized cyclic carbonate and then to copolymerize it with ε-caprolactone. To our knowledge, block copolymers of carboxyl-bearing cyclic carbonates with ε-caprolactone have never been reported.

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The homopolymer and copolymers of ε-caprolactone are usually synthesized by ring-opening polymerization (ROP) of cyclic ester monomers with anionic, cationic, or coordination initiators [28–33] as well as enzymatic catalysts [11,34]. However, anionic initiators such as alkali metal alkoxides lead to significant side reactions, and cationic initiators (such as triethyloxonium tetrafluoroborate and trifluoroacetic acid) or enzymatic catalysts (such as lipases) do not have sufficient efficiency [28,35]. Many coordination initiators for ROP of cyclic esters have been developed such as zinc, iron, titanium, lanthanon, stannous and aluminum etc. But less attention was paid to catalysts or initiators based on group II metals. In our previous papers [36,37], calcium and strontium complexes were successfully applied to the ROP of ε-caprolactone and L-lactide. They exhibited high catalytic activity, low reaction temperature, and high conversion. Especially, they can initiate the block copolymerization of ε-caprolactone with L-lactide, or these two monomers with other cyclic monomers such as ethylene oxide, because the ROP they initiated is a quasi-living polymerization.

Therefore in this paper, 2-methyl-2-benzyloxycarbonyl-propylene carbonate (MBC) was synthesized and its homopolymer (PMBC) and block copolymers with ε-caprolactone (PCL-*b*-PMBC) were prepared via the ring-opening polymerization in the presence of the amino isopropoxyl strontium (Sr-PO) as an initiator. After catalytic hydrogenation, the pendant ester groups were converted to carboxyl groups. They are expected to react with related chemical or bioactive reagents to impart hydrophilicity and bio-affinity, and to facilitate a variety of potential applications in controlled drug delivery, surgery, and tissue engineering.

2. Experimental section

2.1. Materials

Dimethylolpropionic acid (DMPA) and strontium were purchased from Aldrich. Ten percent Palladium on charcoal (10% Pd/C) and benzyl bromide were obtained from corporations in China. ε-Caprolactone (ε-CL, Acros), isopropanol and propylene oxide were dried over calcium hydride. Toluene and tetrahydrofuran (THF) were purified by refluxing over calcium hydride and sodium with the indicator benzophenone complex. Ammonia was dried by a sodium hydroxide column. Amino isopropoxyl strontium (Sr-PO) was prepared according to reference [37].

2.2. Measurements

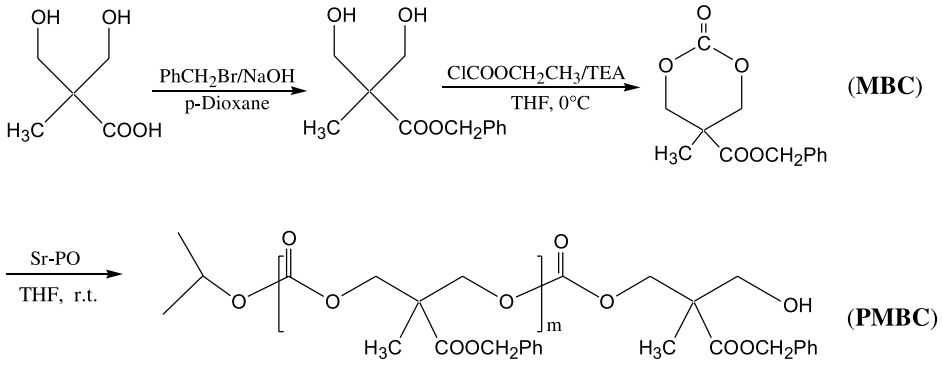
FT-IR spectra were recorded on a Bio-Rad Win-IR instrument. NMR spectra were recorded on a Bruker AV 300 MHz or a Bruker AV 400 MHz in $CDCl_3$ or DMSO at 25 °C. Chemical shifts were given in parts per million from that of tetramethylsilane as internal reference. The GPC measurements were conducted at 35 °C with a Waters 410 GPC instrument equipped with two Waters Styragel columns (HT6E, HT3) and a differential refractometer detector. $CHCl_3$ was used as eluent at a flow rate of 1.0 mL/min. The molecular weights were calibrated against polystyrene standards. X-ray diffractometric analysis was carried out on a Philips apparatus with a Cu Kα (λ = 0.154 nm) source. Thermal analysis was performed using a Perkin–Elmer DSC-7 under N_2 atmosphere at a heating rate of 10 °C/min.

2.3. Synthesis of benzyl 2, 2-bis(hydroxymethyl)propionate (BHP)

Fifty grams (372.8 mmol) of DMPA and 14.9 g (373.0 mmol) of sodium hydroxide were dissolved in 40 mL of water, and the mixture was poured into a large amount of acetone to precipitate the salt formed as a white solid (54.2 g). This product (347.2 mmol) and 41.5 mL (348.3 mmol) of benzyl bromide were added to dioxane (250 mL) as solvent. After 20 h of vigorous stirring at 165 °C, the solvent was removed under reduced pressure and the residue was dissolved in 350 mL of ethyl acetate and extracted with three portions (160×3 mL) of saturated sodium chloride aqueous solution. The combined organic phase was dried with $MgSO_4$ and evaporated to give the diol product as white crystals, 69.4 g, yield: 93.4%; ^{1}H NMR ($CDCl_3$, TMS): δ = 1.10 (s, 3H, –CH_3), 3.52 (d, 4H, –CH_2OH), 5.09 (s, 2H, –CH_2Ar), 7.33 (m, 5H, C$_6H_5$); ^{13}C NMR ($CDCl_3$, TMS): δ = 175.56 (–*C*OO–), 142.65–128.94 (*C*$_6$H$_5$), 68.47 (–*C*H$_2$Ar), 64.69 (–*C*H$_2$OH), 48.17 (*C*–COO), 14.22 (–*C*H$_3$); Elemental Anal. Calcd. for $C_{12}H_{16}O_4$: C 64.3 H 7.19 O 28.5; Found: C 64.1 H 7.29 O 28.6.

2.4. Synthesis of 2-methyl-2-benzyloxycarbonyl-propylene carbonate (MBC)

MBC was prepared by reacting ethyl chloroformate with BHP (Scheme 1) [38]. Firstly, BHP (10.1 g, 40.4 mmol) and ethyl chloroformate (26.0 mL, 0.272 mmol) were dissolved in 250 mL of THF and then, with vigorous stirring, triethylamine (38.0 mL, 0.273 mol) dissolved in THF (70 mL) was added dropwise to the above mixture at 0 °C over a period of 30 min and the reaction was continued at room temperature for another 2 h. Finally, the precipitated triethylamine hydrochloride was filtered off and the filtrate was concentrated under reduced pressure. The residue was recrystallized from THF/ether. White crystals were obtained (yield: 88%). mp: 72–74 °C. ^{1}H NMR ($CDCl_3$ TMS): δ = 1.34 (s, 3H, –CH_3), 4.20 (d, J = 10.8 Hz, 2H, –CH_2O–, 4.71 (d, J = 10.8 Hz, 2H, –CH_2O–), 5.22 (s, 2H, –COOCH_2Ar), and 7.34 ppm (m, 5H, *Ar*). ^{13}C NMR ($CDCl_3$): δ = 17.39 (*C*H$_3$), 40.13 (*C*(CH$_3$)), 67.76 (Ar*C*H$_2$OOC–), 72.84 (–*C*H$_2$OH), 128.45 (ArC), 128.71 (ArC), 134.71 (ArC), 147.36 (*C*COO), 170.88 (O*C*=O). Elemental Anal. Calcd.



Scheme 1. Synthesis and polymerization of 2-methyl-2-benzyloxycarbonyl-propylene carbonate (MBC).

for $C_{13}H_{14}O_5$: C 62.40 H 5.64 O 31.96; Found: C 62.21 H 5.71 O 32.08.

2.5. Homopolymerization of MBC

The MBC monomer (0.363 g, 1.45 mmol) was placed in a dried and degassed glass reactor and the reactor was purged with argon three times. 1.5 mL THF solvent was injected into the reactor with a syringe. Appropriate amount of strontium initiator Sr-PO (9 mg, 0.056 mmol, suspended in 0.5 mL THF) was transferred from its container into the reactor through a rubber tube. The reactor was vigorously stirred and was kept at room temperature for 30 min. The polymerization was terminated by adding a small amount of acetic acid. A small part of the reaction mixture was taken for conversion determination by ^{1}H NMR. The final polymer was isolated by precipitation into cold methanol and by filtration, and was vacuum-dried at room temperature for 24 h. Yield: 97%. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 1.15$ (s, 3H, –CH_3), 4.16 (d, 4H, –CH_2), 5.15 (s, 2H, –CH_2Ar), 7.28 (m, 5H, C_6H_5); IR(film): 1754 ($\nu_{C=O}$ of carbonate), 751 and 697 (δ_{CH} of benzyl group).

2.6. Synthesis of poly(ε-caprolactone-b-2-methyl-2-benzyloxycarbonyl-propylene carbonate) (PCL-b-PMBC)

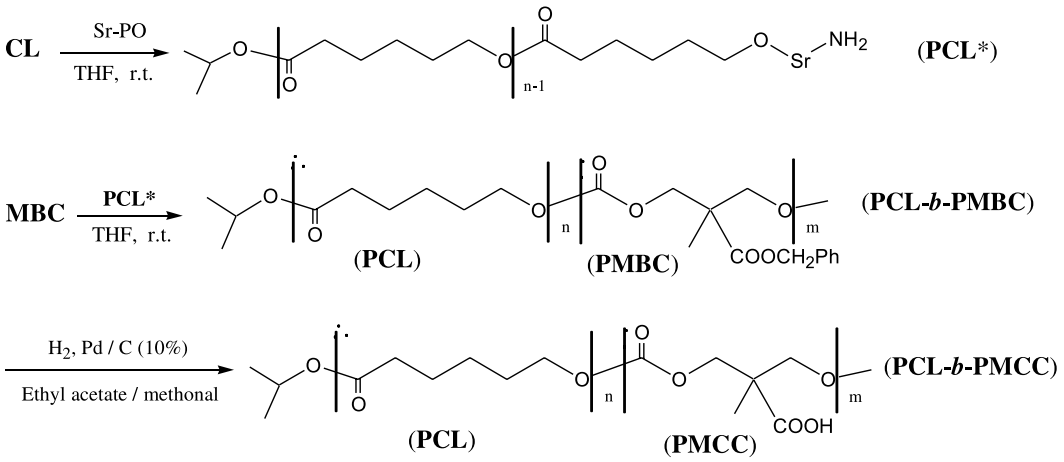
The polymerization was carried out at room temperature. Sr-PO (0.011 g, 0.007 mmol) was added to a dried and argon-purged ampule. THF (2 mL) was then injected by a dry syringe. With vigorous stirring, ε-CL (1.06 g, 9.30 mmol) in 4 mL THF was added. After 30 min of prepolymerization, a part of the reaction mixture was taken for determinations of conversion and molecular weight, and MBC (0.706 g, 2.82 mmol) dissolved in 4 mL THF was added to the remaining part. The polymerization was continued for another 30 min before adding acetic acid to terminate it. The block copolymer was isolated by precipitation as described above. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 1.22$ (3H, –CH_3), 1.39 (2H, C(=O)$CH_2CH_2CH_2CH_2$-CH_2O), 1.65 (4H, C(=O)$CH_2CH_2CH_2CH_2CH_2O$), 2.31 (2H, C(=O)$CH_2CH_2CH_2CH_2CH_2O$), 4.06 (2H, C(=O)CH_2-$CH_2CH_2CH_2CH_2O$), 4.06 (CH_2 in carbonate), 5.13 (s, 2H, –CH_2Ar), 7.34 (m, 5H, $CH_2C_6H_5$); IR(film): 1754 ($\nu_{C=O}$ of carbonate), 1734 ($\nu_{C=O}$ of ε-CL), 751 and 698 (δ_{CH} of benzyl group).

2.7. Deprotection of PCL-b-PMBC

The hydrogenation reaction was conducted by using 250 mL Parr hydrogenator, equipped with a magnetic stirring bar and a programmable temperature controller. The copolymer (0.5 g) was dissolved in THF (24 mL). Ten percent Pd/C (100 mg) suspending methanol (8 mL) and the above solution were added together into the hydrogenator. After purging with argon three times, the reaction mixture was stirred under 1.0 MPa hydrogen pressure at 50 °C for 48 h. And then, the catalyst was removed by filtration and the solution was concentrated by rotary evaporation. The final polymer was precipitated with an excess amount of diethyl ether and dried in vacuum at room temperature over night. ^{1}H NMR (DMSO-d_6, TMS): $\delta = 1.22$ (s, 3H, –CH_3), 1.39 (2H, C(=O)$CH_2CH_2CH_2CH_2CH_2O$), 1.65 (4H, C(=O)$CH_2CH_2CH_2CH_2CH_2O$), 2.31 (2H, C(=O)CH_2CH_2-$CH_2CH_2CH_2O$), 4.06 (2H, C(=O)$CH_2CH_2CH_2CH_2CH_2O$), 4.23 (CH_2 in carbonate); IR(film): 1759 ($\nu_{C=O}$ of carbonate), 1732 ($\nu_{C=O}$ of ε-CL), 3444 (CO–*OH* in carbonate block).

3. Results and discussion

As mentioned previously, many attempts have been made to copolymerize ε-caprolactone with other cyclic esters or carbonates, but functionalized cyclic carbonates have never been used as the comonomer. The aim of the present work is to develop a copolymer of ε-caprolactone and 1, 3-propylene carbonate containing a carboxyl group. The synthetic approach is composed of following three steps as shown in Schemes 1 and 2: (1) to synthesize 2-methyl-2-benzyloxycarbonyl-propylene carbonate (MBC); (2) to polymerize MBC with ε-caprolactone to get block copolymer PCL-*b*-PMBC; (3) to debenzylate PCL-*b*-PMBC to get carboxyl-substituted block copolymer PCL-*b*-PMCC. By



Scheme 2. Preparation and deprotection of block copolymer PCL-*b*-PMBC.

the protection and deprotection of the carboxyl groups, their interference with the synthetic reactions is avoided.

3.1. Preparation of MBC

The MBC was synthesized by a procedure as described by Bisht [38], i.e. through the reaction of ethyl chloroformate with benzyl 2,2-bis(hydroxymethyl)propionate (BHP). This reaction was so effective that the synthetic yield was as high as 88% and the product could be easily purified by recrystalization. The BHP was prepared by reacting the sodium salt of DMPA with benzyl bromide in dioxane at 165 °C as shown in Scheme 1. The reaction yield of this step was 93% because of the use of the BMPA salt [39]. Therefore, the total synthetic yield was better than 80%. As shown by their ^{1}H NMR spectra and elemental analysis data, the BHP and MBC synthesized had desired structures and their purities were high.

3.2. Homopolymerization of MBC

In order to examine the feasibility of using Sr-PO initiator for the copolymerization of ε-CL with MBC, the homopolymerization of MBC by Sr-PO initiator was first investigated. Although the Sr-PO initiator was added as a suspension in THF, the polymerization started as soon as it was mixed with the monomer and soon after the beginning of polymerization, the reaction mixture became homogeneous and transparent. It indicated that when the growing polymer chain had enough length, the Sr initiator, as a part of the growing polymer chain, would dissolve in THF. Within 30 min, the polymerization yield reached 97%, as determined by ^{1}H NMR spectroscopy. The number-average molecular weight (Mn) and molecular weight distribution index (MWD) determined by GPC were 1.3×10^4 and 1.49, respectively. The Mn was in agreement with that calculated from monomer/initiator ratio in the feed. The ^{1}H NMR spectrum and its peak assignment of PMBC are shown in Fig. 1. The main peaks marked with letters a to d can be assigned to the corresponding hydrogen atoms of PMBC. The minor peaks at 1.27 and 5.30 ppm are associated the isopropyl end group originating from the Sr-OP initiator. This means that the ROP of MBC had the same mechanism as that of ε-caprolactone or lactide as proposed in our previous papers [36,37]. The PMBC polymer could be dissolved in THF and could be precisely characterized by ^{1}H NMR and FT-IR spectroscopy. This would facilitate the subsequent synthesis and characterization.

3.3. Synthesis of block copolymer PCL-b-PMBC

In our previous paper [33], block copolymer PCL-*b*-PLLA was prepared by using Sr-PO as initiator. Because MBC can be polymerized by Sr-PO, the similar sequential ROP was employed to synthesize PCL-*b*-PMBC. That is,

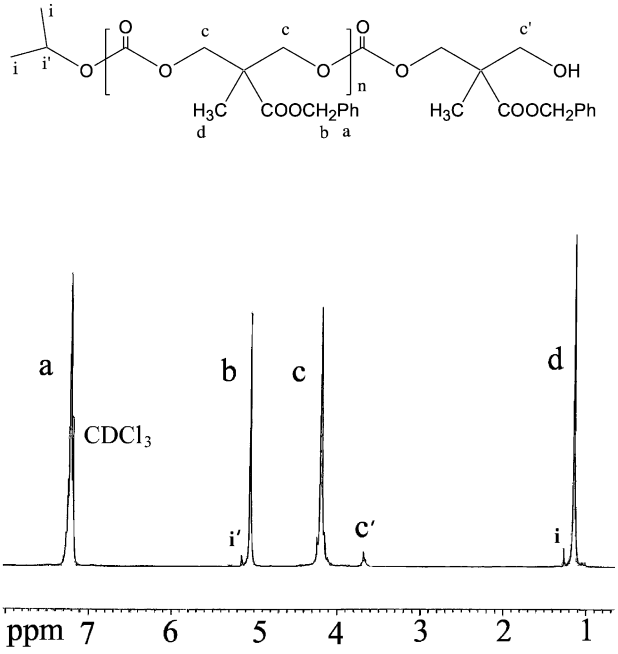


Fig. 1. ^{1}H NMR spectrum of PMBC and its peak assignment.

ε-CL was first polymerized in THF at room temperature using Sr-OP as initiator for 30 min, and then MBC was added to the reactor to continue the polymerization. After termination and precipitation, the block-copolymer PCL-*b*-PMBC was obtained. By changing the ε-CL/MBC ratio and Sr-PO/ε-CL ratio, different block copolymers were prepared (Table 1). The total polymer yields were around 98%. The GPC curves of the prepolymer PCL and the copolymers all exhibited a single peak, indicating that the final products were the block copolymer rather than a mixture of homopolymers. Taking PCL3 and PCL-*b*-PMBC3 as an example, their Mn's were 3.8×10^4 and 5.6×10^4 g/mol, respectively. The MWD of the copolymer (1.28) was even narrower than PCL3 (1.50). Their GPC results are shown in Fig. 2. Figs. 3 and 4 show ^{1}H NMR spectra of PCL oligomer and PCL-*b*-PMBC1, respectively. It could be seen that all main peaks of PCL (Fig. 3) and PMBC (Fig. 1) appeared in Fig. 4. In the FT-IR spectra (Fig. 6), the δ_{CH} characteristic peaks of the benzyl group appeared at 751 and 698 cm^{-1} in addition to all peaks of PCL. All the above evidence confirmed the formation of PCL-*b*-PMBC block copolymers. That means that the living PCL chain was an efficient macroinitiator for the polymerization of MBC, in agreement with the result in Ref. [37].

3.4. Deprotection

The benzyl protecting groups of the PCL-*b*-PMBC were easily removed by catalytic hydrogenolysis over Pd/C (10%) in anhydrous ethyl acetate/methanol. Notably, in order to avoid the inactivation of the catalyst due to polymer wrapping, the polymer must be completely dissolved in ethyl acetate by heating and ultrasonic treatment, and the polymer solution and the Pd/C suspension in anhydrous methanol were added together into the hydrogenator. The debenzylation of PCL-*b*-PMBC was performed under 1.0 MPa H_2 atmosphere at 50 °C for 48 h. Almost all benzyl groups were removed, as evidenced by the absence of the resonances at 5.13 ppm (CH_2Ar) and 7.34 ppm (*Ar*) in the ^{1}H NMR spectra (Fig. 5) and the disappearance of the δ_{CH} vibrations of benzyl group at 751 and 698 cm^{-1} in the FTIR spectra (Fig. 6). In addition, the OH stretching band centered at 3444 cm^{-1} was strengthened tremendously after hydrogenolysis due to the formation of pendant COOH groups.

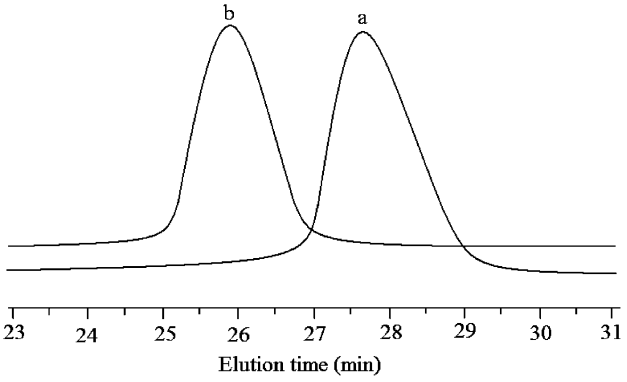


Fig. 2. GPC traces of (a) PCL3 ($M_n=3.8\times10^4$, MWD=1.50) and (b) PCL-*b*-PMBC3 ($M_n=5.6\times10^4$, MWD=1.28).

3.5. X-ray Diffraction

The crystallizability of PCL-*b*-PMBC block copolymers can be discussed on the basis of WAXD patterns depicted in Fig. 7. PMBC did not show any diffraction peaks and was completely amorphous. The homopolymer PCL was highly crystalline and exhibited an intense peak at $2\theta=21.2°$ and two smaller ones at 21.8 and 23.6°. These diffraction peaks of PCL were all observed in PCL-*b*-PMBC, but their intensity became weaker with increasing PMBC content. It indicated that the presence of PMBC block in PCL-*b*-PMBC influenced the crystallizability of the PCL segments. After debenzylation, the diffraction peaks were hardly observed in PCL-*b*-PMCC (Fig. 8). This was attributed to the formation of the COOH groups in PCL-*b*-PMCC. The hydrogen bonds could be formed not only between the carboxyl groups in PMCC segments, but also between the carboxyl groups in PMCC blocks and the ester groups in PCL blocks. These latter inter-block interactions, especially the inter-molecular hydrogen-bonding hampered the crystallization of PCL segments.

Table 1
Copolymerization of ε-CL and MBC initiated by Sr-PO

Polymer	X_{MBC}(%)[a]	$M_n(10^4)$[b]	M_w/M_n[b]	Yield (%)[c]	T_g(°C)	T_m(°C)
PCL3	–	3.8	1.50	99	n.d.	58.3
PMBC	–	1.3	1.49	97	8.80	–
PCL-*b*-PMBC1	14.7	8.5	1.45	99/96	−49.3	57.0
PCL-*b*-PMBC2	21.7	4.6	1.47	98/96	−45.6	55.9
PCL-*b*-PMBC3	41.7	5.6	1.28	99/97	−30.8	54.6
PCL-*b*-PMBC4	50.0	1.3	1.56	99/97	−21.7	52.1

The polymerization was carried out in THF at room temperature in the presence of Sr-PO as initiator.

[a] X_{MBC} is the molar content of MBC units in the copolymer estimated from ^{1}H NMR spectra (300 MHz, $CDCl_3$).

[b] Determined by GPC ($CHCl_3$ as eluent).

[c] Estimated from ^{1}H NMR spectra (300 MHz, $CDCl_3$) of the final reaction mixture; '99/96' represented the polymerization yields of ε-CL and MBC, respectively.

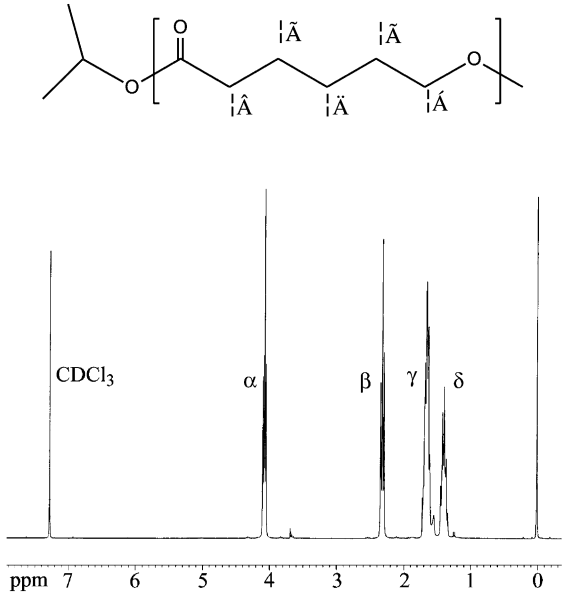


Fig. 3. ^{1}H NMR spectrum of PCL oligomer and its peak assignment.

3.6. Thermal properties

The DSC curves of PCL-*b*-PMBC are shown in Fig. 9. The homopolymer PCL is a highly crystalline material and has a melting temperature (T_m) at 58.3 °C and a crystallization temperature (T_c) of 32.1 °C. The homopolymer PMBC is an amorphous polymer and has a glass transition temperature (T_g) at 8.8 °C. A T_m was observed in all PCL-*b*-PMBCs from 57 to 52 °C, decreasing with increasing PMBC content. The melting enthalpy ΔHm was lower than that of PCL homopolymer. It implied that the crystallinity and the crystal perfectness of the PCL blocks were lowered due to the presence of PMBC segments. The glass transition (T_g) in PCL-*b*-PMBC was examined by DSC. As shown in Table 1,

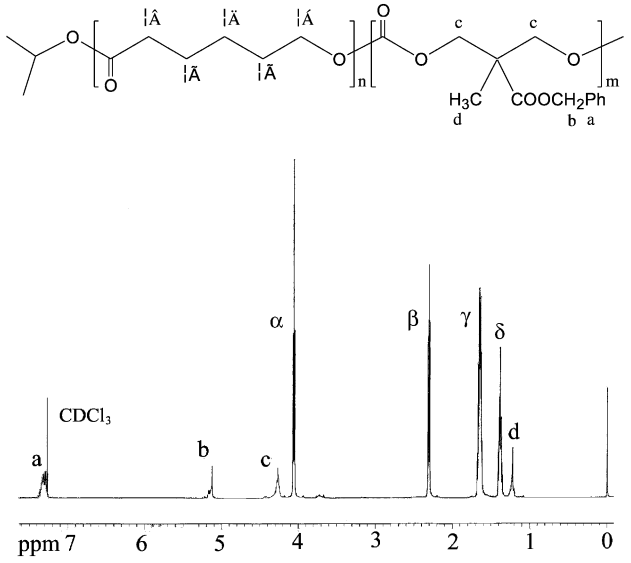


Fig. 4. ^{1}H NMR spectrum of PCL-*b*-PMBC1 and its peak assignment.

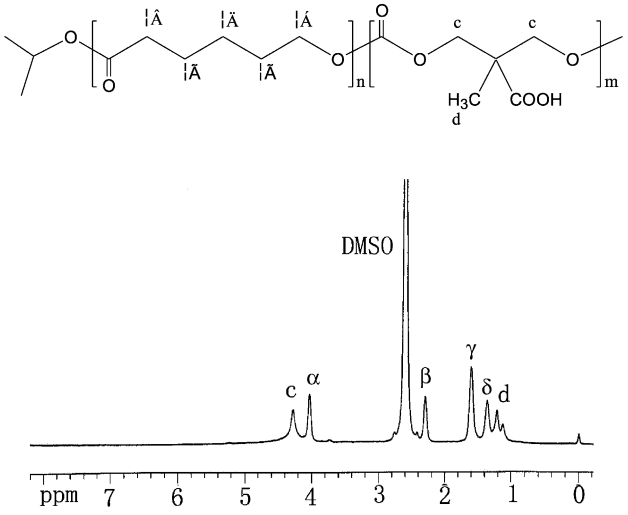


Fig. 5. ^{1}H NMR spectrum of PCL-*b*-PMCC1 and its peak assignment.

PCL-*b*-PMBC exhibited a T_g in the range of −41.6 to −23.3 °C, increasing with increasing PMBC content. It showed that there were strong interactions between the PMBC blocks and PCL blocks although they were not entirely miscible. The immiscibility is because PCL is highly crystalline, the PCL segments become separated from the PMBC segments and crystallized themselves. But in the amorphous domains, PCL and PMBC blocks are mixed together and strong interactions may exist between the both because there are obvious structure similarity and dipole–dipole interactions between the two blocks. After debenzylation, the ΔHm of PCL-*b*-PMC was 10.9 J/g compared to 68.0 J/g of PCL-*b*-PMBC (shown in Fig. 10). This indicated that crystallinity of PCL-*b*-PMC decreased dramatically, in agreement with the WAXD results.

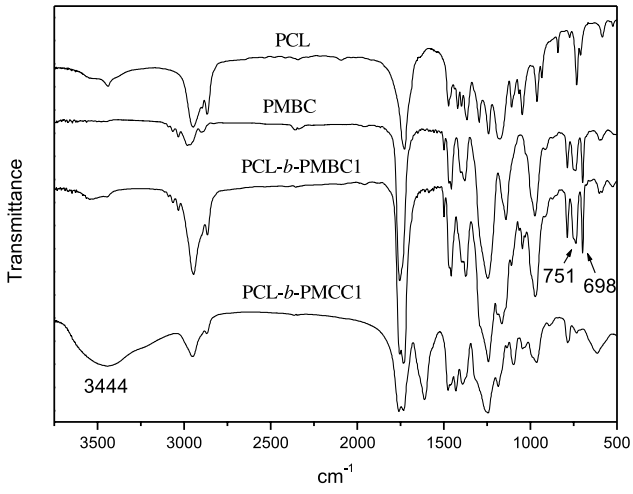


Fig. 6. Infrared spectra of PCL, PMBC, PCL-*b*-PMBC1 and PCL-*b*-PMCC1.

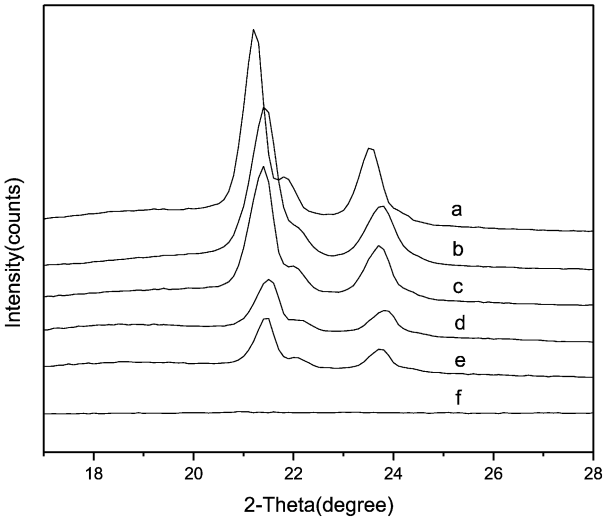


Fig. 7. WAXD curves of (a) PCL, (b) PCL-*b*-PMBC1, (c) PCL-*b*-PMBC2, (d) PCL-*b*-PMBC3, (e) PCL-*b*-PMBC4 and (f) PMBC.

4. Conclusions

Block copolymers PCL-*b*-PMBCs were prepared by sequential ring opening polymerization of ε-CL and MBC. An amino isopropoxyl strontium (Sr-PO) initiator was employed to perform this reaction under mild conditions. The diffraction peaks of homo-PCL were all observed in the WAXD of PCL-*b*-PMBC, and their intensity became weaker as the length of the PMBC block increased relatively to the PCL block. DSC results showed that PCL-*b*-PMBC had a T_m from 52 to 57 °C and T_g from −42 to −23 °C, indicating the strong interactions between the two blocks. Debenzylation of PCL-*b*-PMBC by catalytic hydrogenation led to the block copolymer PCL-*b*-PMCC with pendant carboxyl groups. Diffraction peak of PCL-*b*-PMCC was hardly observed and ΔHm of PCL-*b*-PMCC was only 10.9 J/g compared to 68.0 J/g of PCL-*b*-PMBC. It meant that the presence of carboxyl groups dramatically lowered the crystallinity of the PCL blocks, probably due to the formation of hydrogen bonds between the PCL and PMCC blocks.

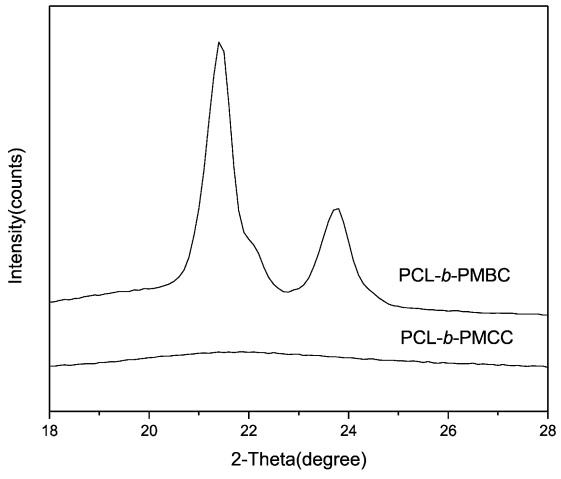


Fig. 8. WAXD curves of PCL-*b*-PMBC1 and PCL-*b*-PMCC1.

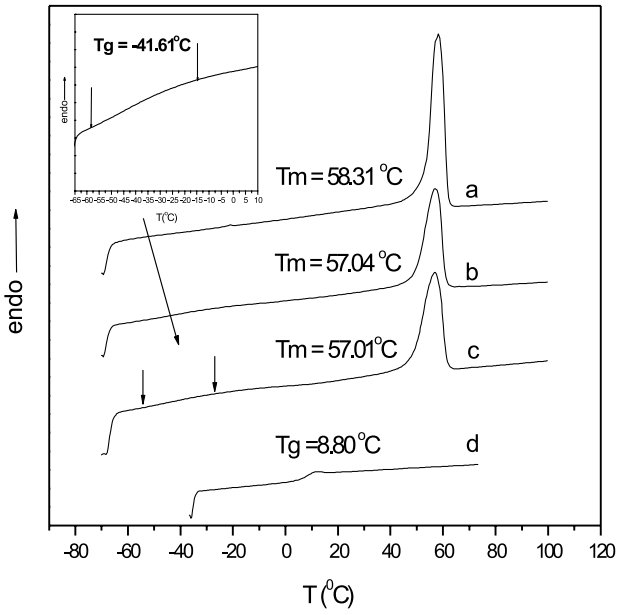


Fig. 9. DSC thermograms of (a) PCL (second heating run); (b) PCL-*b*-PMBC1 (second heating run); (c) PCL-*b*-PMBC1 (third heating run after quenching); (c) PMBC (second heating run).

Presence of the pendant carboxyl groups on PCL-*b*-PMCC copolymer is expected to enhance the biodegradability of the polymers and to facilitate further modifications of the polymer, such as attaching drug molecules, short peptides and oligosaccharides onto the carboxyl groups. Further investigation is in progress and will be reported elsewhere.

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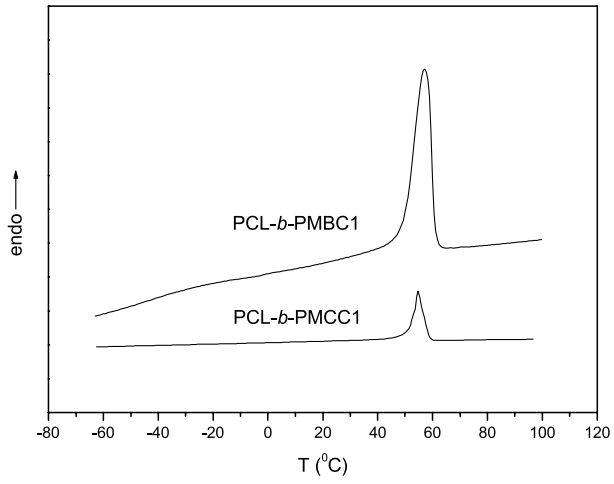

Fig. 10. DSC thermograms of (a) PCL-*b*-PMBC1 (ΔHm = 68.0 J/g); (b) PCL-*b*-PMC1 (ΔHm = 10.9 J/g) for the second heating run.

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