Synthesis and ring-opening polymerization of *α*-chloromethyl-*α*-methyl-*β*-propiolactone

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SUMMARY: *α*-Chloromethyl-*α*-methyl-*β*-propiolactone (CMMPL) was synthesized by dehydrohalogenation of *α*,*α*-dichloromethyl-*β*-propionic acid which was obtained by chlorination of *α*,*α*-hydroxymethyl-*β*-propionic acid (DMPA). Due to high strain of the four-numbered ring, CMMPL can be polymerized by ring-opening with or without an initiator. Both electrophiles like trifluoroacetic acid (TFAA) and nucleophiles like triethylamine (TEA) and pyridine, as well as organometallic compounds such as stannous octoate [$Sn(Oct)_2$)], aluminium triisopropoxide [$Al(O^iPr)_3$] and tetrabutyl orthotitanate [$Ti(OC_4H_9)_4$], were found to be effective initiators. The polymerization can be conducted by either solution or bulk polymerization. P(CMMPL) is insoluble in almost all organic solvents at room temperature. An endothermic peak (ca. 214 ∼ 250 °C) attributed to the melting transition of P(CMMPL) was observed in DSC curves. P(CMMPL) tends to have high crystallinity (40% ∼ 60%) as demonstrated by its X-ray diffraction patterns, and the crystallinity was found to vary with the types of initiator used.

Introduction

Aliphatic polyesters have been widely used as biomedical materials and environmentally degradable thermoplastics[1–3]. These aliphatic polyesters are often prepared by either polycondensation of diols with diacids or ring-opening polymerization of lactones. In polycondensation reactions, it is usually difficult to achieve high molecular weight even if the polymerization yield is close to 100%. The ring-opening polymerization has been found to be more useful and efficient.

In general, aliphatic polyesters do not have many pendant functional groups (other than end groups) to allow chemical modification altering their properties or to conjugate with drugs, therefore the application of these polyesters is limited.

A new kind of aliphatic polyester containing functional pendant groups, mainly derived from natural malic acid or trifunctional amino acids, has been studied continuously[4–13]. These polymers exhibit good hydrophilicity and rapid hydrolytic degradation rates in comparison to other types of aliphatic polyesters without functional side groups. However, a few problems still remain to be resolved, such as limited availability of functional groups, the complexity and low yield associated with the synthesis of functional monomers, expensive starting material, and less controllable copolymerization. These problems, to some extent, have slowed down the investigation and limited their practical application. Till now, the investigations have been concentrated mainly on the synthesis and characterization of functional aliphatic polyesters containing pendant carboxyl or amino groups, at least in part, due to their easy modification and non-toxicity of their degradation products. However, there are only a few reports in the literature on aliphatic polyesters containing halo-substituted pendant groups that can also be modified[14].

In this paper, we discuss the synthesis of *α*-chloromethyl-*α*-methylpropiolactone (CMMPL) prepared by successive chlorination, hydrolysis and lactonization of a commercially available material, i.e., 2,2′-bis(hydroxymethyl)propionic acid (DMPA). The ring-opening polymerization was studied by using several types of initiators such as trifluoroacetic acid (TFAA), triethylamine (TEA), pyridine, $Sn(Oct)_2$, $Al(O^iPr)_3$, $Ti(OC_4H_9)_4$ and without any initiators. The thermal properties and crystallinity of the P(CMMPL) were also studied.

Experimental part

Materials

Bis(2,2′-hydroxymethyl)propionic acid (DMPA), stannous octoate [$Sn(Oct)_2$], aluminium triisopropoxide [$Al(O^iPr)_3$] and tetrabutyl orthotitanate [$Ti(OC_4H_9)_4$] were purchased from Aldrich Chemical Co. and purified by distillation under reduced pressure before use. Triethylaluminium/toluene solution (0.051 M) was provided by Dalian Institute of Chemical Physics, Academic Sinica. Trifluoroacetic acid (TFAA) from Aldrich was used as received. Triethylamine (TEA), pyridine, *N*-methyl-2-pyrrolidone (NMP) and the solvents used for the polymerizations were purified in accordance with the standard methods. All other reagents were analytical grade and used without further purification.

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Monomer synthesis

α,α′-Bis(chloromethyl)propionic acid (DCMPA): The reaction was carried out in a three-neck flask. A condenser was connected with a NaOH solution trap to absorb the hydrogen chloride generated from the reaction. 13.4 g (0.1 mol) of 2,2′-bis(hydroxymethyl)propionic acid (DMPA), 59.5 g (0.5 mol) of thionyl chloride ($SOCl_2$) and a few drops of DMF were charged in the flask. The mixture was stirred vigorously at room temperature for about 18 h and then refluxed for about 24 h until no HCl was evolved. Excess $SOCl_2$ was removed by distillation under reduced pressure. After the residue was cooled to 0 °C, a certain amount of distilled water was added dropwise under vigorous stirring till the complete hydrolysis of *α,α′*-bis(chloromethyl)propionyl chloride. The oily layer was separated, and the water layer was extracted three times with diethyl ether. The combined mixture of oily layer and diethyl ether was dried with anhydrous $MgSO_4$ overnight. After removing diethyl ether, the residue was recrystallized twice from petroleum ether, and white crystals were obtained with a melting point of 61 ∼ 63 °C. The total yield was 87%.

^1H NMR ($CDCl_3$, TMS): δ = 1.44 (s, 3H, $-CH_3$), 3.75, 3.91 (d + d, 2H + 2H, $-CH_2Cl$), 11.5–12.2 (broad, 1H, $-COOH$).

MS: m/z = 155 (M^+-CH_3), 135 (M^+-Cl), 121 (M^+-CH_2Cl).

IR (KBr): 3200–3000 ($-COOH$), 2980 (CH_2, CH_3), and 1740 cm^{-1} ($C{=}O$).

$C_5H_8Cl_2O_2$ (171.02)	Calc.	C 35.12	H 4.71	Cl 41.46
	Found	C 36.63	H 4.99	Cl 41.00

α-Methyl-α-chloromethyl-β-propiolactone (CMMPL): To a cooled solution of 17.1 g (0.1 mol) of DCMPA in 60 ml of chloroform was slowly added 50 ml of KOH (0.1 mol) aqueous solution with strongly stirring till the pH reached 6.8. The mixture was maintained under vigorous stirring at 50 °C for about 1 h. After cooling, the chloroform layer was separated from the mixture, then another portion of chloroform (60 ml) was added into the water layer, and the same procedure was repeated for two more times. The combined chloroform layer was washed three times with water, then dried with anhydrous $MgSO_4$ overnight. The crude lactone was obtained by distillation at 45–47 °C/0.2 mmHg after removing chloroform. The monomer was further purified by twice distillation under reduced pressure over CaH_2 prior to polymerization.

^1H NMR ($CDCl_3$, TMS): δ = 1.55 (s, 3H, $-CH_3$), 3.59–3.81 (q, 2H, $-CH_2Cl$), 4.12–4.46 (q, 2H, $-CH_2O-$).

MS: m/z = 135 (M^+-Cl), 104 (M^+-COOH).

IR (NaCl): 2980 ($-CH_2$, $-CH_3$), 1820 ($C{=}O$), and 1124, 1091 cm^{-1} ($-COC-$).

$C_5H_7ClO_2$ (134.56)	Calc.	C 44.63	H 5.24	Cl 26.35
	Found	C 45.07	H 5.44	Cl 26.22

Polymerization

The polymerizations of CMMPL were carried out in a previously flamed and dry argon-purged tube at a given temperature for a certain interval of time. The solvent, monomer and initiator were added carefully via a rubber septum with a syringe, and the polymerization tubes were degassed for 10 min and sealed under vacuum. The white products were dissolved into hot NMP, precipitated into methanol, isolated by filtration and dried in vacuo at 50 °C for 48 h.

Methods

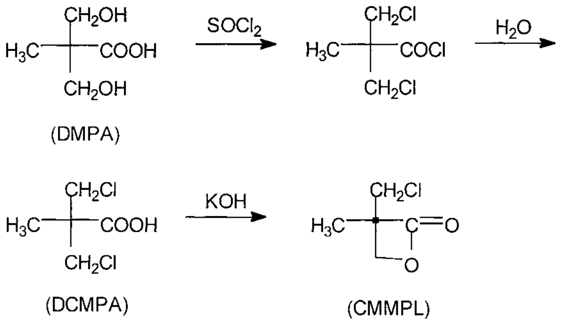
^1H NMR spectra of monomer and intermediates were recorded on a Bruker ARX400 spectrometer, and chemical shifts in parts per million (ppm) are reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference. Infrared spectra (IR) were recorded on a Nicolet Magna IR-750 spectrophotometer. Mass spectra were obtained with a VG ZAB-HS mass spectrometer (EI). Elemental analyses were carried out using a Perkin-Elmer 204 elemental analyzer. Differential scanning calorimetry (DSC) measurements were performed on a Shimadzu DSC-50 at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was recorded on a Shimadzu DT-30 at a heating rate of 20 °C/min under nitrogen. X-ray diffraction patterns were obtained on a Rigaku D/max 2000 diffractometer. The Cu-K_α radiation was used from a Siemens generator operating at 40 kV and 100 mA, and a graphite monochromator was utilized in front of the detector (λ = 0.154 nm). Measurements were made in the 2θ range from 4–70° at a rate of 4.000 degree/min with 0.02° intervals.

Results and discussion

Monomer synthesis

Several types of lactones containing functional groups have been reported[4, 10)], however, the functional groups such as carboxyl or amino groups must be protected before polymerization and then be de-protected after polymerization. The procedure is laborious with low yields. By comparison, CMMPL can be readily obtained with high yield by chlorination of bis(2,2′-hydroxymethyl)propionic acid with $SOCl_2$, followed by hydrolysis and lactonization with KOH as described in Scheme 1.

Scheme 1: Synthesis of CMMPL



Though the synthetic method to CMMPL via chlorination of valerolactone (VL) with chlorine in the presence of a chlorination promoter was reported in a patent$^{15)}$, and the method from 4-keto-1,3-dioxane was briefly mentioned in other reports$^{16,17)}$, no detailed characterization of the monomer was reported. The present method is first reported in this lab to the best of our knowledge. The structure of the monomer was well characterized, and the whole process is easily controllable. The chloromethyl groups will serve as a potential active site for further modification.

Polymerization

Like other β-lactones$^{18)}$, CMMPL can be polymerized in bulk using different types of initiators, i.e., anionic initiators like TEA and pyridine, Lewis acids like TFAA, and organometallic compounds such as $Sn(Oct)_2$, $AlEt_3$ and $Al(O^iPr)_3$. The polymerization was also conducted without adding any initiator. The polymerization results are listed in Tab. 1.

Anionic polymerization of CMMPL initiated by TEA and pyridine takes place at room temperature with high polymer yield, while the other polymerizations, initiated by TFAA, organometallic compounds and thermal polymerization, must be carried out at higher temperature, see Tab. 1. P(CMMPL) is almost insoluble in common solvents at room temperature. Although it can be dissolved in hot hexamethylphosphoramide (HMPA), hexafluoro-2-propanol, NMP and *o*-dichlorobenzene at temperatures over 100 °C, it is quite difficult to prepare a solution of P(CMMPL) for determining its molecular weight with an Ubbelohde viscometer at these extreme conditions. It can be seen from Tab. 1 that P(CMMPL) made via $Sn(Oct)_2$ initiation shows higher melting temperature and enthalpy, indicating higher crystallinity of these P(CMMPL)s. We thus studied the solution polymerization of CMMPL using $Sn(Oct)_2$ as an initiator. The results are summarized in Tab. 2.

Tab. 1. Bulk polymerization of CMMPL initiated by different initiators and T_m and ΔH_f of the P(CMMPL) obtained

Exp. No.$^{a)}$	Initiator	Polym. temp. in °C	Yield in %	$\frac{T_m}{°C}$	$\frac{\Delta H_f}{J/g}$
1	$Sn(Oct)_2$	60	92	249.9	53.8
2	Pyridine	25	96	245.8	52.2
3	TEA	25	90	242.3	40.2
4	TFAA	60	55	240.9	39.9
5	$AlEt_3$	60	90	237.8	45.0
6	$Al(O^iPr)_3$	60	92	235.6	41.2
7$^{b)}$	–	90	74	214.4	20.5

[a] Polymerization condition: [M]/[I] = 500 (molar ratio), 24 h.

[b] Polymerized without initiator for 48 h.

Tab. 2. Polymerization of CMMPL in chlorobenzene initiated by $Sn(Oct)_2$ $^{a)}$

Exp. No.	Solvent	Dielec. const. (ε)	Temp. in °C	Yield in %	$\frac{\eta_{inh}}{dl/g}$ $^{b)}$
1	Benzene	2.2	70	31	0.21
2	Toluene	2.4	60	–	
3	Toluene	2.4	90	29	0.18
4	Chlorobenzene	5.7	60	–	
5	Chlorobenzene	5.7	90	63	0.44
6	Chloroform	7.6	60	37	0.27
7	*o*-Dichlorobenzene	9.9	90	52	0.22

[a] [M]/[Cat.] = 500 (molar ratio), [M] = 0.2 mol/L, polymerization time 24 h.

[b] Determined by using an Ubbelohde viscometer and NMP at 30 ± 0.1 °C.

In solution polymerization, the mixture was homogeneous initially. As the polymerization continued, the solution turned turbid. At 60 °C, the solution polymerization of CMMPL in toluene or chlorobenzene did not occur, while in chloroform the polymer yield is only as low as 37%. At 90 °C, CMMPL can be polymerized in toluene, chlorobenzene and *o*-dichlorobenzene, and the yields of P(CMMPL) are observed to gradually increase with the increase of dielectric constants of solvents used for polymerization. It is probably due to that the ring-opening polymerization of CMMPL initiated by $Sn(Oct)_2$ occurs via a coordination-insertion mechanism. In non-polar or low polar solvents, $Sn(Oct)_2$ tends to form aggregates, resulting in lower initiating efficiency. Increasing the polarity of solvents, on the other hand, can prevent aggregation of $Sn(Oct)_2$ to some extent, and thus results in higher polymer yield.

The precipitated P(CMMPL) exhibited a very low solubility in common solvents at room temperature, but was soluble in part in NMP. The viscosities listed in Tab. 2 are the results of only the soluble parts of P(CMMPL) in NMP determined by Ubbelohde viscometer at 30 ± 0.1 °C. It is also shown in Tab. 2 that, for the NMP-soluble part of P(CMMPL), its molecular weight is highest when chlorobenzene was used as the polymerization solvent. This observation promoted us to investigate the time-dependent polymer yield in chlorobenzene using different initiators at 90 °C, and the results are shown in Fig. 1.

It can be seen that at room temperature the solution polymerization of CMMPL initiated by pyridine or TEA is faster than those initiated by organometallic compounds at 90 °C, and the overall polymerization rate of CMMPL initiated by these initiators is in the following order: pyridine, TEA > $AlEt_3$, $Al(O^iPr)_3$, $Sn(Oct)_2$, $Ti(OBu)_4$ > TFAA.

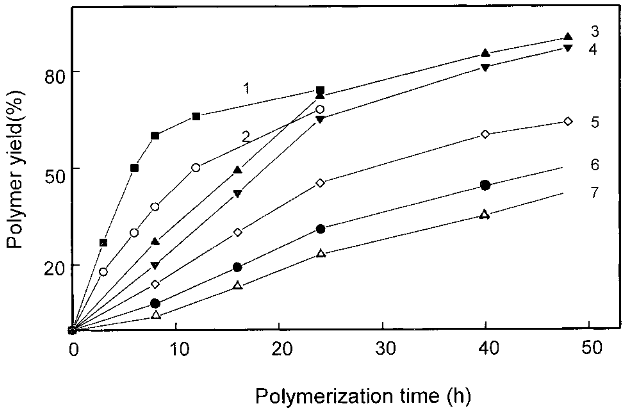


Fig. 1. Time-yield plots of the polymerization of CMMPL initiated by various types of initiators in chlorobenzene at 90 °C. [M]/[I] = 500 (molar ratio), [M] = 2.46 mol/L, initiators: (1) pyridine, carried out at room temp., (2) TEA, carried out at room temp., (3) AlEt$_3$, (4) Al(O^{i}Pr)$_3$, (5) Sn(Oct)$_2$, (6) Ti(OBu)$_4$, (7) TFAA

Characterization of P(CMMPL)

Fig. 2 shows the IR spectra of both CMMPL and P(CMMPL). In general, for highly strained cyclic compounds, the IR adsorption bands of endocyclic bonds shift to lower wavenumber, while those of exocyclic bonds exhibit at relatively higher wavenumber. As shown in Fig. 2, due to the strain in the four-numbered ring, the carbonyl absorption band of P(CMMPL) shifts to 1739 cm^{-1}, while that of the monomer appears at 1824 cm^{-1}. At the same time, the —C—O—C— absorption band of P(CMMPL) shifts to 1110 cm^{-1}, 1175 cm^{-1} from 1091 cm^{-1}, 1124 cm^{-1} of that of the monomer. The characteristic peaks of *β*-lactone at 1824 cm^{-1} and 911 cm^{-1} disappeared after polymerization.

The ^{1}H NMR spectra of CMMPL and of the chloroform-soluble fraction of P(CMMPL), along with assignments, are given in Fig. 3. In CMMPL, the well-defined splitting of the peaks at δ = 3.59 ppm ~ 3.81 ppm are corresponding to the two protons of —CH$_2$Cl, while those at 4.12 ppm ~ 4.46 ppm are of —CH$_2$O—. In P(CMMPL), the chemical shift due to —CH$_3$ shifts to δ = 1.34 ppm from δ = 1.55 ppm in CMMPL; —CH$_2$Cl, and —CH$_2$O— appear in the same chemical shift range as those in CMMPL, but the splitting of all the peaks is more complicated due to the complexity of polymer chain tacticity.

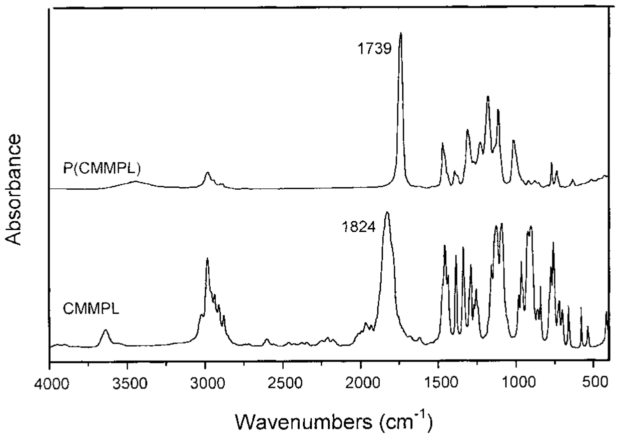


Fig. 2. FT-IR spectra of CMMPL and P(CMMPL)

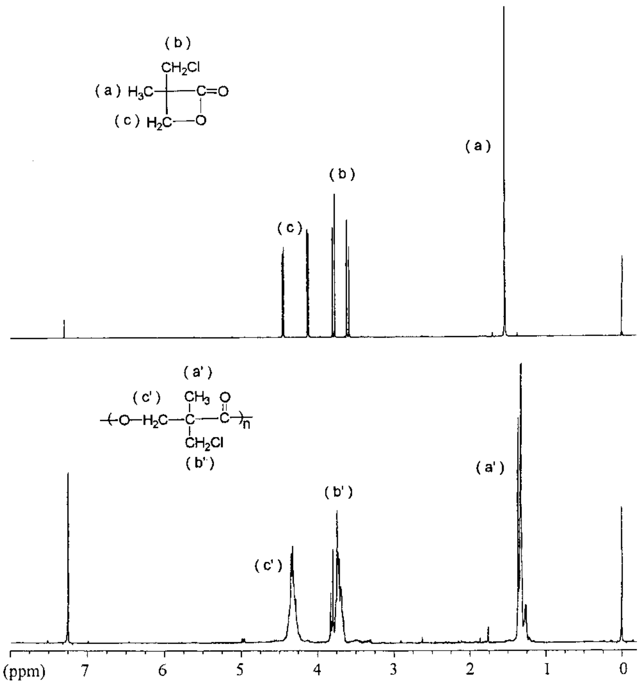


Fig. 3. ^{1}H NMR spectra of CMMPL and of the chloroform-soluble fraction of P(CMMPL)

The thermal properties of the P(CMMPL) samples as described in Tab. 1 were studied by TGA and DSC. All P(CMMPL) samples decompose around 320 °C. The DSC results are shown in Fig. 4. It is clearly seen that only one endothermic peak was observed from −100 to 300 °C, no clear glass transition was observed, even though the polymer sample was quenched in liquid nitrogen from the molten state. All P(CMMPL) samples prepared by using initiators show sharper melting transition than that obtained without using any initiator. The melting points (T_m) and the enthalpies (ΔH_f) of P(CMMPL) obtained by bulk polymerization with different initiators are listed in Tab. 1; they are all affected by the initiators used. P(CMMPL) samples obtained from thermal polymerization show the lowest melting point and heat of fusion.

It has been reported that the glass transition temperature (T_g) of P(CMMPL) is 63 °C[19)], but no detailed information about the sample preparation and methods of measurement was given. The fact that no glass transition was observed in the above samples in our lab is, at least in part, due to the relatively low molecular weight of P(CMMPL). The crystallization is too fast to allow the measurement of T_g even when the P(CMMPL) samples are quenched in liquid nitrogen from molten state.

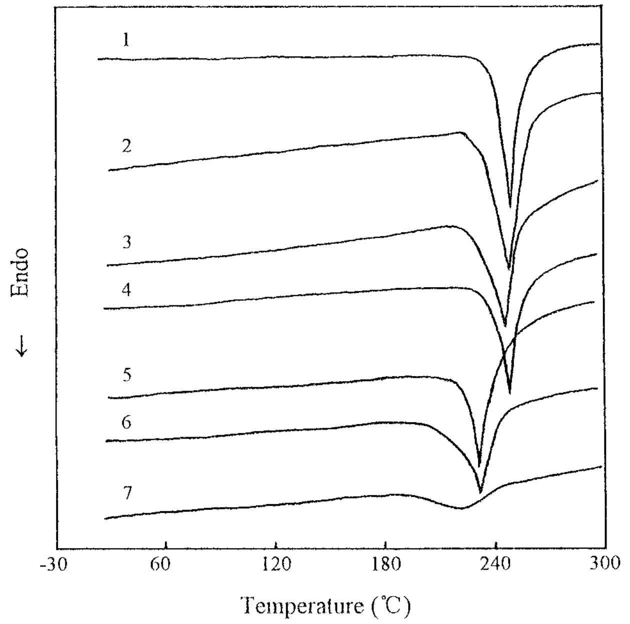


Fig. 4. DSC traces of P(CMMPL); the samples are the same as described in Tab. 1

In order to determine the T_g value of P(CMMPL), a new initiator, 1,3-dichlorotetrabutyldistannoxane, was synthesized according to the literature[20]. It is reported that this initiator can effectively induce the ring-opening polymerization of lactones to get high molecular weight polyesters[21]; in addition, it forms solid crystals and is easy to handle. Thus, two new samples of P(CMMPL) were prepared by using 1,3-dichlorotetrabutyldistannoxane as an initiator (sample A: [M]/[I] = 2000 mol/mol; sample B: [M]/[I] = 4000 mol/mol).

Fig. 5 shows the DSC curves of the first scan and the second scan of these two samples. The first scan was recorded from –100 °C to 280 °C with a heating rate of 10 °C/min. No glass transition could be detected, and only melting temperatures (231.7 °C for sample A and 240.5 °C for sample B) were observed. After the first scan, the molten sample was immediately quenched by liquid nitrogen and then used for the second scan. A glass transition temperature was observed at –8.0 °C for sample A and −4.3 °C for sample B. The cold crystallization takes place at 19.6 °C for sample A and 30.1 °C for sample B from the glassy states, respectively. The melting temperatures were virtually the same as in the first scan. In order to clearly display the glass transition, the two scans in Fig. 5 are drawn in different temperature ranges.

Our T_g values of P(CMMPL) are rather low compared with the literature value of 63 °C, which may have resulted from different polymerization conditions and polymer sample preparation. However, the relatively low transition temperatures obtained in our work are similar to one of the two glass transitions of poly(pivalolactone) (ca. −10 °C and 170 °C)[22].

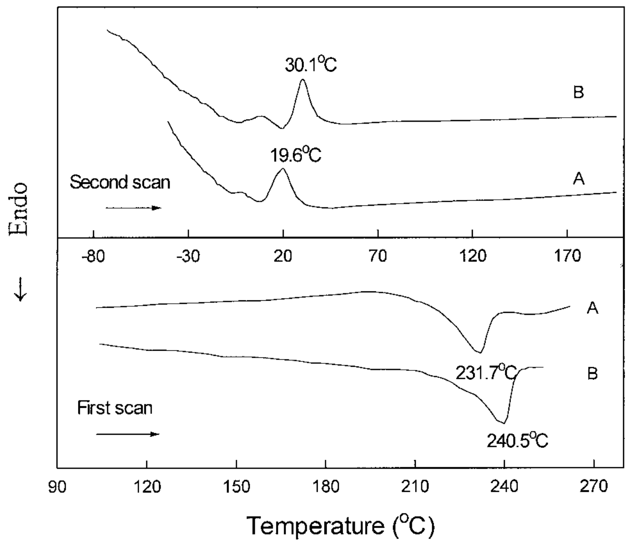


Fig. 5. DSC traces of P(CMMPL) obtained by using 1,3-dichlorotetrabutyldistannoxane as an initiator in bulk (A: [M]/[I] = 2000 (molar ratio); B: [M]/[I] = 4000 (molar ratio))

It is known that the temperature difference between cold crystallization temperature (T_c) and T_g, i.e., $\Delta T = T_c - T_g$, reflects the crystallization behavior of a certain type of polymer. The smaller the ΔT value, the easier the polymer tends to crystallize. As for the above two samples of P(CMMPL), the ΔT values are 27.6 °C for sample A and 34.4 °C for sample B, respectively, which means that sample A is easier to crystallize than sample B. Since sample B was obtained by using less amount of initiator than for sample A, this result also supports the conclusion that P(CMMPL) with lower molecular weight is easier to crystallize.

Fig. 6 shows the X-ray diffraction patterns of the P(CMMPL) samples as described in Tab. 1. Like poly(pivalolactone) and poly(3-hydroxybutyrate)[22,23], P(CMMPL) also exhibits the characteristic diffraction patterns of a typical polymer with high crystallinity. P(CMMPL)s prepared by using different initiators display almost the same diffraction pattern, which indicates that they have the same crystalline structure. The major diffraction peaks at $2\theta = 15.360°$, $17.120°$ and $21.840°$ correspond to d-spacings of 5.7638 Å, 5.1751 Å and 4.0661 Å, respectively. The degree of crystallinity of P(CMMPL) was estimated to be in the range of 40 ~ 60%.

Conclusion

α-Chloromethyl-α-methyl-β-propiolactone (CMMPL) was synthesized by dehydrohalogenation of α,α-bis(chloromethyl)-β-propionic acid (DCMPA). DCMPA was obtained by chlorination of α,α-bis(hydroxymethyl)-β-propionic acid (DMPA) which is readily available commercially. P(CMMPL)s were made by ring-opening poly-

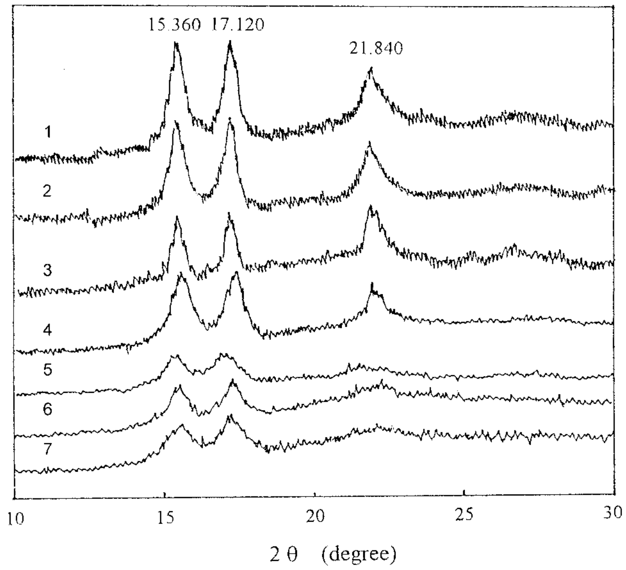


Fig. 6. X-ray diffraction patterns of P(CMMPL); the samples are the same as described in Tab. 1

merization of CMMPL in bulk or in solution initiated by various types of initiators. These polymers are difficult to dissolve in common organic solvents at room temperature and have high melting points. P(CMMPL) has high crystallinity as indicated by X-ray diffraction patterns as well as by the huge melting peak in DSC curves. The low solubility can be attributed, at least in part, to the high crystallinity of P(CMMPL). The copolymerization of CMMPL with other cyclic monomers, such as ε-caprolactone (CL), lactide (LA), and glycolide (GL), is currently underway. The preliminary results indicate that the pendant chloromethyl groups can readily be converted to quaternary ammonium salts by reacting the polymer with a tertiary amine. The main-chain structure of the copolymer is not affected, and the hydrophilicity of the copolymer is improved.

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