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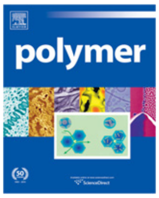

Controllable preparation of poly(alkylene carbonate)s and observation on their structure-related odd–even effect

Wei Su, Jun Feng*, Hua-Fen Wang, Xian-Zheng Zhang, Ren-Xi Zhuo

Key Laboratory of Biomedical Polymers of Ministry of Education & Department of Chemistry, Wuhan University, Wuhan 430072, PR China

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ABSTRACT

The primary aim of this paper is to explore the influence of the number of CH_2 groups per $–(CH_2)_nOCOO–$ repeat unit (Num_c) on the properties of poly(alkylene carbonate)s. A series of poly(alkylene carbonate)s with different Num_c, including PTMC ($Num_c = 3$), PTeMC ($Num_c = 4$), PPMC ($Num_c = 5$), PHMC ($Num_c = 6$) and PDMC ($Num_c = 10$) were investigated for that purpose by DSC and XRD techniques. The method of $Sn(Oct)_2$-catalyzed ring-opening polymerization was developed to prepare poly(pentamethylene carbonate)s (PPMC), which presented a controllable feature. Regarding crystallization rate and *Tm* of poly(alkylene carbonate)s, an interesting odd–even effect was first reported related to the Num_c. The order of crystallizing ability of poly(alkylene carbonate) was: PTMC ($Num_c = 3$) < PPMC($Num_c = 5$) < PTeMC ($Num_c = 4$) < PHMC ($Num_c = 6$) < PDMC ($Num_c = 10$). Poly(alkylene carbonate)s characterized with even Num_c appeared to readily crystallize relative to that with odd Num_c.

1. Introduction

The past two decades have witnessed a growing public and scientific concern regarding the use of biodegradable plastic material as a solution for the problem of plastic waste. Among biodegradable polymers aliphatic polyesters and polycarbonates have attracted considerable attention due to their combination of biodegradability, biocompatibility and physical or chemical properties. [1–3]. Several biodegradable polymers, represented by poly(caprolactone) (PCL), polylactide (PLA), poly(glycolic acid) (PGA) and poly(trimethylene carbonate) (PTMC), have been successfully developed to meet the specific demands, e.g., in agriculture, packaging and pharmaceutical industries. Relative to polyesters, polycarbonates can degrade by a surface erosion process without the formation of acidic degradation compounds [4–6]. This is especially attractive to the environmental conservation and *in vivo* medical application. Furthermore, polycarbonates have much lower degradation rate than polyesters [4], which would be advantageous in the applications where relatively higher stability is desired.

To meet the demands for different purpose, synthetic polycarbonates with versatile properties are required. At present, the synthesis of cyclic carbonates has become an important method towards polycarbonates preparation. As demonstrated, ring-opening polymerization (ROP) of cyclocarbonates seems of the most effective method to fabricate polycarbonates with good reproducibility and high quality (high molecular weight and low polydispersity). More attractively, by design, polycarbonate copolymers with a wide variety and accurate controllability in the physical and mechanical properties are readily provided via facile ring-opening copolymerization. However, in addition to PTMC, the reports concerning the ring-opening preparation and properties of poly(alkylene carbonate)s are limited within PTeMC, PHMC, POMC and PDMC derived from 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol and 1,10-decanediol, respectively [7–17].

Because the crystal structure and morphology are responsible for many properties of the final polymer products, the knowledge of the crystallization is crucial for designing materials with the required properties. Based on the comparison on the crystallization behavior of PTMC, PTeMC, PHMC, POMC and PDMC [15,17], Kricherdolf group previously educed that poly(alkylene carbonate)s having more CH_2 groups per repeat unit of $–(CH_2)_nOCOO–$ should possess more rapid crystallization rate. It appears difficult to understand why PTMC does not crystallize at all although it has just one less CH_2 group than PTeMC which is semi-crystallizing. It should be noted that all the referred polycarbonates contain even number of CH_2 groups per repeat unit (Num_c) except PTMC. Nevertheless, for aliphatic polyesters, polyamides and polyimides, an odd–even effect in the properties related to Num_c have been found [18–20]. May be there also exists the odd–even effect stemmed from polycarbonate structure and it would exert some

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* Corresponding author. Tel./fax: +86 27 6875 4509.
E-mail address: fengjun@whu.edu.cn (J. Feng).

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influences on the crystallization properties? However, to our best knowledge, no efforts have been devoted to address this issue regarding the structure–property relationship. And high molecular weight polycarbonates with odd Num_c have not been reported up to now except for PTMC.

With those in mind, the present paper reported the investigation of the thermal properties of poly(alkylene carbonate)s with different chain length by means of DSC and WAXD techniques. To acquire a systematic understanding about the structure–property relationship, controllable ring-opening preparation of poly(pentamethylene carbonate) (PPMC), containing five CH_2 groups per repeat unit ($Num_c = 5$), was achieved. Whereas some patents have been devoted to the preparation of PPMC, low molecular weight oligomers were the main products via polycondensation method [21–24]. Its synthesis by ring-opening polymerization has never been reported and a fundamental characterization is also missing. Therefore, another purpose of this work is to broaden the research of PPMC and fabricate high molecular weight polymers to meet the different demands.

2. Experimental

2.1. Materials

Toluene was dried over Na/K alloy and distilled before use. 1,5-Pentanediol was purchase from Fluka and used directly. Stannous octoate ($Sn(Oct)_2$) and diethyl carbonate was of chemical grade from Beijing Chemical Plant. $Sn(Oct)_2$ was purified by distillation under reduced pressure and dissolved in dry toluene for further use.

2.2. Instrumentation

Melting point determinations were performed on a microscopic (20 × 10) melting point apparatus and were uncorrected. FD mass spectrum was recorded on a JEOL JMS-700 (MStation). IR spectra were recorded on a Perkin–Elmer-2 spectrometer. Samples were film-cast in chloroform onto sodium chloride plates. ^1H NMR spectra were recorded in a solution of $CDCl_3$ on a Varian Mercury-VX 300 apparatus with TMS as internal standard. Gel-permeation chromatography (GPC) was carried out on a Waters HPLC system equipped with a Model 2690D separation module, a Module 2410 differential refractive index detector and a Shodex K803 column. Chloroform was used as eluent at a flow-rate of 1.0 mL/min. Waters MILLIENIUM32 module software was used to calculate molecular weights based on a universal calibration curve generated by narrow molecular weight distribution polystyrene standards. The sample concentration and injection volume was 0.3% (wt/v) and 20 μL, respectively. Differential scanning calorimetry (DSC) measurements were carried on a Perkin–Elmer DSC 7 thermal analyzer. Samples of 8 ± 0.1 mg were used in test and sealed in aluminium pans. The sample was heated and cooled in most tests at the rate of 10 °C/min. If some other rate was used this will be discussed in the specific section. The glass-transition temperature (T_g) was taken as the midpoint of the heat capacity increment associated with the glass-to-rubber transition. The melting temperature (T_m) was determined as the peak value of the endothermal phenomenon in the DSC curve. The same holds for the crystallization temperature (T_c) determination. The heat of fusion (ΔH_m) of the crystal phase was calculated from the area of the DSC endotherm. The wide angle X-ray scattering (WAXS) powder patterns were recorded with a transmission powder diffractometer XRD-6000 (Shimadzu, Japan) with Cu K_α radiation of 1.5406 Å. The data were collected in the 2θ range from 10 to 80° in 18 min. A 1° divergence and 1° antiscatter slits were used. Samples were film-cast in chloroform and kept at 35 °C for 10 days.

2.3. Synthesis of dimeric monomer cyclobis(pentamethylene carbonate)

The cyclocarbonate derived from 1,5-pentanediol was synthesized for the purpose to prepare high molecular weight PPMC via ROP. The method through thermal degradation of oligomers was performed similar to the reference [16]. The distilled crude product was washed with cold methanol (−10 °C). The solid residue was recrystallized from ethyl acetate for four times to isolate the monomer product named as cyclobis(pentamethylene carbonate) $(PMC)_2$. Yield 30%, m.p. 119–120 °C. Mass spectroscopy revealed a peak of 259 g/mol proving the dimeric nature of the monomer. IR: $\nu = 1744\ cm^{-1}$ (C=O). ^1H NMR ($CDCl_3$): $\delta = 4.21–4.26$ (t, $OC\underline{\mathbf{H}_2}$, 4H), 1.65–1.68 (m, $OCH_2C\underline{\mathbf{H}_2}$, 4H), 1.47–1.52 (m, $OCH_2CH_2C\underline{\mathbf{H}_2}$, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 155.5$ ($\underline{\mathbf{C}}O$), 67.8 ($O\underline{\mathbf{C}}H_2CH_2$), 29.8 ($OCH_2\underline{\mathbf{C}}H_2CH_2$), 22.4 ($OCH_2CH_2\underline{\mathbf{C}}H_2$).

2.4. Preparation of poly(pentamethylene carbonate) (PPMC)

All reactions were carried out in bulk (Scheme 1). A typical preparation of PPMC was conducted as follows: $(PMC)_2$ was introduced to a thoroughly cleaned and dried glass flask which was pretreated with Me_2SiCl in toluene. $Sn(Oct)_2$ solution was transferred by syringe. The vessel was vacuumed (60 Pa) to remove toluene and purged with argon. Then the vessel was sealed in vacuo and immersed into oil bath thermostated at determined temperature for a period of time. The obtained products without any treatment were dissolved in a determined amount of $CHCl_3$ (0.3% (wt/v)) and directly used for the GPC measurements to determine the monomer conversion in addition to the molecular weight and polydispersity.

One part of the resulting product solution in $CHCl_3$ was concentrated and then poured into excessive menthol as a poor solvent. The isolated polymer was dried in vacuo to constant weight for IR or NMR analysis. IR: $\nu = 1743\ cm^{-1}$ (C=O). ^1H NMR ($CDCl_3$): $\delta = 4.11–4.20$ (t, $OC\underline{\mathbf{H}_2}$, 4H), 1.65–1.75 (m, $OCH_2C\underline{\mathbf{H}_2}$, 4H), 1.41–1.52 (m, $OCH_2CH_2C\underline{\mathbf{H}_2}$, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 155.5$ ($\underline{\mathbf{C}}O$), 67.8 ($O\underline{\mathbf{C}}H_2CH_2$), 29.5 ($OCH_2\underline{\mathbf{C}}H_2CH_2$), 22.5 ($OCH_2CH_2\underline{\mathbf{C}}H_2$).

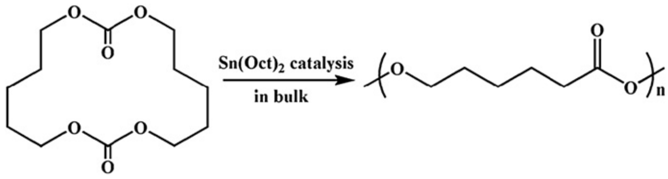
2.5. Preparation of poly(alkylene carbonate) samples

Poly(alkylene carbonates) derived from 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol and 1,10-decanediol, name as PTMC (Yield 40%), PTeMC (Yield 20%), PHMC (Yield 11%) and PDMC (Yield 10%), were prepared using the similar method as described for PPMC preparation [14–17]. Before molecular and thermal characterization, all the polymers were carefully purified by dissolution in chloroform and precipitation in cold methanol. The M_n of the samples used in this paper was 5.2×10^4 (PTMC), 6.0×10^4 (PPMC), 4.9×10^4 (PTeMC), 5.1×10^4 (PHMC) and 5.3×10^4 g/mol (PDMC) with the polydispersity in the range of 1.1–1.3.

3. Results and discussion

3.1. Monomer preparation

To prepare poly(pentamethylene carbonate) (PPMC) with high molecular weight via ROP, the cyclocarbonate derived from 1,5-



Scheme 1. Synthesis of PPMC via ring-opening polymerization of $(PMC)_2$.

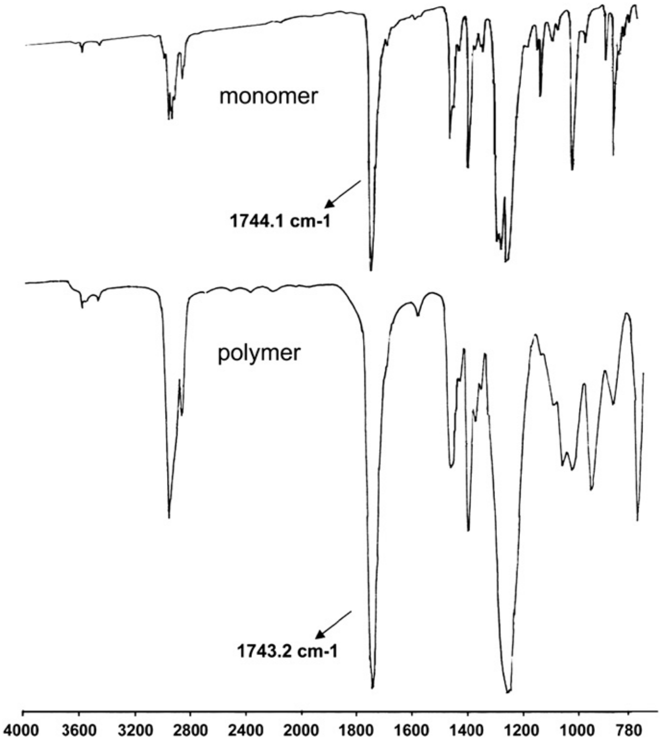


Fig. 2. IR spectrum of (PMC)$_2$ and PPMC.

pentanediol was synthesized. In general, the synthesis of cyclocarbonates involves two methods: 1) thermal decomposition of corresponding oligomers in vacuo; 2) direct cyclization using α,ω-alkanediol to react with ethyl chloroformate or phosgene analogues [2]. In this paper, NMR, IR and MS analysis demonstrated that dimeric cyclobis(pentamethylene carbonate) (PMC)$_2$ other than monomeric PMC was obtained through thermal decomposition method, which was consistent with the reference reported [25,26].

When dealing with 1,3-propanediol and 1,4-butanediol by direct cyclization method, monomeric TMC and tetramethylene carbonate (TeMC) were readily provided in high yield [11,27–29]. Similar successful synthesis of monomeric cyclocarbonate from longer α,ω-diol has not been described till now, whereas dimeric cyclocarbonates derived from 1,6-, 1,8-, 1,10-diols have been synthesized [14,15,17]. In this work, the attempt for monomeric PMC preparation also failed by reacting 1,5-pentanediol with ethyl chloroformate or triphosgene. It is supposed that the ability to form monomeric cyclocarbonate exhibits a decreasing tendency with increasing length of α,ω-diol. The farer the distance of the two terminal groups in α,ω-diol molecules, the more difficult the intramolecular back-bitting reaction to form cyclic carbonate. Consequently, occurrence of the competitive intermolecular reaction is favorable, providing linear polymers.

To our knowledge, a spectroscopic characterization of both (PMC)$_2$ and PPMC has never been published before. The ^{13}C and ^{1}H NMR spectra showed that the characteristic signals of (PMC)$_2$ and PPMC are slightly different (Fig. 1). Meanwhile the IR spectra of (PMC)$_2$ displays a “C=O” band at a wavelength of 1744.1 cm^{-1} which is almost identical with that of PPMC at 1743.2 cm^{-1} (Fig. 2). The similarity in the spectroscopy between dimeric cyclocarbonate and corresponding polymer was also found for cyclobis(tetramethylene carbonate) (TeMC)$_2$ and poly(tetramethylene carbonate) (PTeMC) from 1,4-butanediol [16]. However, the monomeric TeMC displayed a distinct hypsochromic shift relative to PTeMC. As known, TeMC is subject to spontaneous melting therm-polymerization while dimeric (TeMC)$_2$ are more stable and unchanged even at 180 °C. Those marked deviation somewhat implied that relative to monomeric carbonates, dimers may suffer much less ring-strain, and adopt the molecular conformation more close to that of linear polycarbonates. Thus the formation of (PMC)$_2$ as the main products during the severe thermal degradation can be explained to be thermodynamically favorable. This also applied to the cases when therm-decomposing the oligomers from 1,4-, 1,6-, 1,8-, 1,10-diols, since their thermo-decomposition product are mainly dimeric carbonates [14–17]. Nevertheless, the thermo-decomposition of the oligomers from 1,3-propanediol resulted in monomeric TMC yet rather than dimeric (TMC)$_2$ [30]. Obviously it is insufficient to explore the therm-degradation merely from the thermodynamic perspective since large-sized (TMC)$_2$ appears of lower ring-strain.

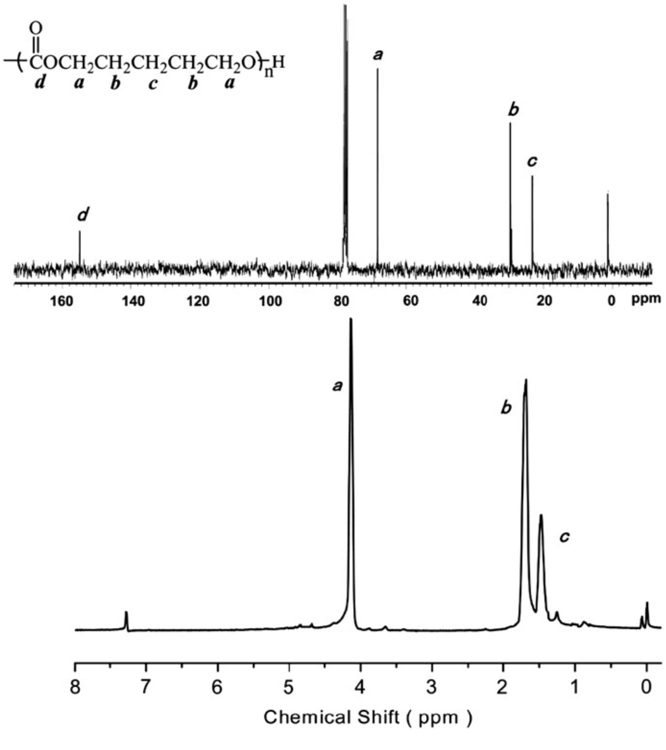


Fig. 1. ^{13}C and ^{1}H NMR spectra of PPMC with the M_n of 6.94 × 10^4 g/mol.

3.2. Polymer synthesis and characterization

Sn(Oct)$_2$ is a widely used catalyst for ROP of cyclocarbonates [13] and approved for internal application by FDA. In consideration of the application potential of PPMC in medical field, Sn(Oct)$_2$ catalysis was applied to PPMC preparation and proved to be a high-efficient method with respect to high molecular weight (up to 1.7 × 10^5 g/mol) of resulting polymers. As the control, no occurrence of bulky polymerization was observed without catalyst addition. It strongly demonstrated that Sn(Oct)$_2$ catalysis is the indispensable factor for the polymerization. The polymerization of cyclocarbonates sometimes involved partial decarboxylation thus leading to the formation of poly(alkylene ether–carbonate) with a significant content of ether units [30]. ^{1}H NMR spectra of the resulting PPMC demonstrated that no decarboxylation occurred since no signal at around 3.45 ppm belonging to the ether group (–CH$_2$–O–C$\mathbf{H_2}$–) [31] could be detected (Fig. 1).

All the data concerning Sn(Oct)$_2$-catalyzed polymerization are summarized in Table 1. It was observed that at the later stage during the polymerization, the monomer conversion intended to

Table 1
Conditions and Results of bulky ring-opening polymerization of $(PMC)_2$ initiated with $Sn(Oct)_2$[a].

Entry	Reaction temperature (°C)	$[Sn(Oct)_2]$[b]	Time (h)	$M_n \times 10^{-4}$ (g/mol)[c]	M_w/M_n[c]	Conversion (%)[c]
1	125	250:1	7	8.36	1.55	61
2	125	250:1	10	9.41	1.63	97
3	125	250:1	14	9.82	1.69	97
4	125	250:1	18	6.94	1.73	97
5	125	100:1	10	3.04	1.89	98
6	125	500:1	10	13.02	1.73	57
7	125	500:1	19	17.06	1.27	94
8	160	250:1	3.5	9.84	1.40	99

[a] The polymerizations were performed with the constant $(DMC)_2$ amount of 0.1 g.
[b] molar ratio of $(PMC)_2/Sn(Oct)_2$.
[c] determined by GPC using $CHCl_3$ as eluent.

remain constant, with a slight decrease in product M_n (Table 1, entries (1–4)). It suggested that the chain growth process may be followed by a backbiting degradation due to the transesterification. As shown in Table 1, the lower the $(PMC)_2/Sn(Oct)_2$ molar ratio, the shorter the reaction time was to attain the quantitative conversion (Table 1, entries (3, 5, 7)). The variation of $(PMC)_2/Sn(Oct)_2$ ratio also exerted tremendous effect on the product M_n. The polymerizations at the ratio of 100, 250 and 500 produced PPMC with maximum M_n of 3.04×10^4, 9.82×10^4 and 17.00×10^4 g/mol, respectively. As shown in Fig. 3, the plot of M_n versus molar feed ratio of $(PMC)_2/Sn(Oct)_2$ appears to fit the linear regression line with a correlation coefficient (r^2) of 0.995. It suggested that a stoichiometric reaction between $Sn(Oct)_2$ and $(PMC)_2$ may occur. Meanwhile, ^{1}H NMR spectra of PPMC clearly demonstrated the existence of the CH_2–OH and octoate endgroups (Fig. 4). Therefore, $Sn(Oct)_2$ was more possible to play a role of initiator and the polymerization exhibited controllable feature. Relatively higher temperature (for example, at 160 °C) was found to help shorten the reaction time to attain quantitative conversion (Table 1, entry 8).

$Sn(Oct)_2$-catalyzed solution polymerization in toluene was also attempted for PPMC preparation. No polymer was obtained while a great amount of $(PMC)_2$ crystal emerged after cooling the reaction system, irrespective of the variation in $Sn(Oct)_2$ concentrations. In contrast, for the bulky or solution polymerization of TMC, both the polymerizations proceeded successfully and high yield of PTMC was obtained [13,32,33]. Due to the instability of TMC at high temperature leading to thermal spontaneous polymerization [34], the two cases might be indeed not comparable.

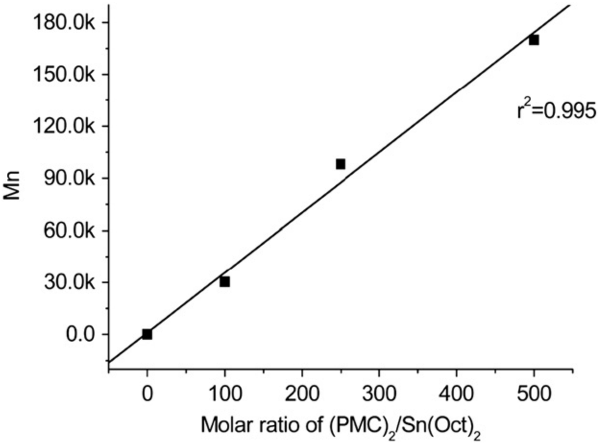


Fig. 3. Relationship between M_n and molar feed ratio of $(PMC)_2/Sn(Oct)_2$.

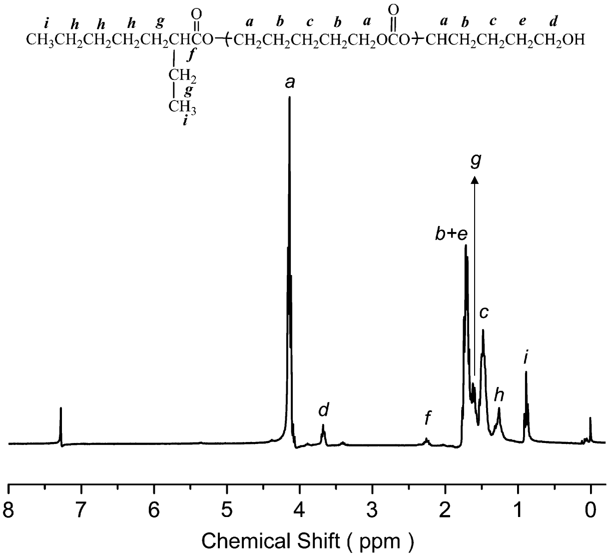


Fig. 4. ^{1}H NMR spectra of PPMC obtained under the condition (molar ratio of $(PMC)_2$ to $Sn(Oct)_2$ was fixed at 10, polymerization time of 24 h).

3.3. Comparative investigation on poly(alkylene carbonate) properties

The structure–property relationship is discussed based on the comparative investigation on the crystallization behaviors of poly(alkylene carbonate)s with different number of CH_2 groups per repeat unit (Num_c), including PTMC ($Num_c = 3$), PTeMC ($Num_c = 4$), PPMC($Num_c = 5$), PHMC ($Num_c = 6$), PDMC ($Num_c = 10$). It was observed by us that PPMCs with different M_ns (3.0×10^4, 6.0×10^4, 13.0×10^4 g/mol) have the similar DSC curve and, the related characteristic data for three samples appears to depend little on the M_ns within the measuring range. Similar finding were previously reported in PTeMC study [14]. Furthermore, since all the data came from the samples characterized with similar M_ns, the influence of the molecular weight on the properties can be excluded in this work. It is well established that the melting behavior of a polymer is affected by its previous thermal history and therefore, in order to provide the same heat treatment to all the samples investigated, prior to thermal analysis the samples were aged for 10 days.

The characteristic DSC data of those investigated polycarbonates were summarized in Table 2. As can be seen, both T_m and T_g are affected by the chemical structure of the polycarbonates. A glass-transition behavior at −40 °C of PPMC was detected in DSC curve. T_g of the poly(alkylene carbonate)s display a decreasing trend as the Num_c increased. This result can be explained on the basis that the higher the Num_c, the lower the concentration of the stiffer carbonate

Table 2
DSC data of polycarbonates with different Num_c.

	Num_c[a]	T_g (°C)[b]	T_{m1} (°C)[b]	T_{m2} (°C)[c]	δH_m (J/g)[b]	T_c (°C)[b]
PDMC	10	−41	62	60	77.13	40
PHMC	6	−42	54	52	39.94	3
PPMC	5	−40	46	–[d]	17.44	–[d]
PTeMC	4	−36	56	–[d]	48.46	–[d]
PTMC	3	−15	–[d]	–[d]	–[d]	–[d]

[a] number of $(CH)_2$ groups per repeat unit of $–(CH_2)_nOCOO–$.
[b] The data was afforded from the DSC measurement in the first scan(Heating and cooling rates, 10 °C/min).
[c] The data was afforded from the DSC measurement in the second scan(Heating rates, 10 °C/min).
[d] undectected.

groups. As a result, the polymeric chain is more flexible and thus the polymer has a lower T_g.

As far as the DSC traces (first scan) of the room-stored samples are concerned, they are typical semicrystalline material, being characterized by the presence of a conspicuous melting endotherm. Nevertheless, the T_m did not show a one-way variation with $\mathrm{Num_c}$ increasing as expected. DSC measurement of PPMC revealed a melting endothem peaked at 45 °C, whereas those of PTeMC, PHMC and PDMC were much higher. The variation of δH_m with $\mathrm{Num_c}$ increasing is similar to that for T_m. After melt quenching, the phase behavior of the samples under investigation appears to be much different: as reflected from the DSC traces (Fig. 5), PPMC and PTeMC samples were relatively slowly crystallizing materials which did not crystallize when quenched and reheated at a rate of 10 °C/min, whereas corresponding melting endotherm was distinctly detectable in the seconding heating curve of PHMC and PDMC. Interestingly, after melting quenching by slow cooling (−10 °C/min) and annealing for 1.5 h at 30 °C, a significant degree of crystallinity is detectable again for PTeMC, whereas PPMC was found to be still amorphous, as evidenced by the absence in its DSC curve of a melting endotherm (Fig. 5). DSC heating curves of PPMC with different annealing time was shown in Fig. 5. As shown, long enough annealing process for more than 24 h has to be required before detecting a weak crystallinity again for PPMC samples after melting quenching; a narrower melting endotherm peak with much higher intensity and Tm value would be observed when prolonging the annealing process to 96 h, indicating that longer annealing would be beneficial for the perfection of PPMC's crystallinity. Those DSC results strongly suggested that PPMC crystallizes more slowly than PTeMC, PHMC and PDMC. In fact, commercialized PHMC materials, named as "APC-POLYOLS", is highly crystallizing and PPMC block has been used to introduced into PHMC chains by transesterification reaction resulting in the marked improvement of the flexibility, elasticity and the ability to spin [35,36]. In order to compare the crystallizing rate of PHMC and PDMC, four cooling course with different cooling rate (−10 to −80 °C/min) was employed. It was found that at a cooling rate of −80 °C/min the crystallization of PHMC can be quite suppressed. A relatively weak supercooling effect was found for PDMC since corresponding crystallization exotherm was still observed in the cooling curve (−80 °C/min). Taking into account the fact that PTMC is amorphous, the order of crystallizing ability of poly(alkylene carbonate) was: PTMC ($\mathrm{Num_c} = 3$) < PPMC($\mathrm{Num_c} = 5$) < PTeMC ($\mathrm{Num_c} = 4$) < PHMC ($\mathrm{Num_c} = 6$) < PDMC ($\mathrm{Num_c} = 10$). As a matter of fact, crystallization rates almost follow the order of T_m of the polycarbonates discussed above.

Kricherdolf group previously educed that poly(alkylene carbonate)s having larger $\mathrm{Num_c}$ possess more rapid crystallization rate. It should be noted that this deduction is conflicting to the result observed by us since as reported here, PTeMC are more readily crystallizing than PPMC. The deviation may find an explanation based on the fact that all the polycarbonates investigated by Kricherdolf group including PTeMC, PHMC, POMC and PDMC were characterized by even $\mathrm{Num_c}$. As known, for aliphatic polyesters, polyamides and polyimides, there exists remarkable odd–even effect in the properties related to $\mathrm{Num_c}$ [18–20]. Thus a proposition was naturally brought up that an odd–even effect related to the $\mathrm{Num_c}$ should be responsible for the retardation in PPMC crystallization compared to PTeMC. The odd–even effect for poly(alkylene carbonate)s is also partly reflected from the T_m fluctuation with the increasing $\mathrm{Num_c}$.

To check the structure of the crystalline phase in the samples under investigation and to correlate it to the chemical structure, further experiment by using X-ray diffractometry were performed at room temperature. The diffraction curves for PTeMC, PPMC and PDMC are reported in Fig. 6. Since corresponding profiles of PHMC and PDMC are very similar to each other, that of PHMC was not shown here. Although the crystal structure was not discussed in this paper, some important information can be provided. It can be noted that PTeMC X-ray diffraction profile closely resembled that of PDMC and PHMC: the X-ray profiles of those aliphatic polycarbonates with an even $\mathrm{Num_c}$ are indeed characterized by a low angle reflection ($2\theta = 16.96°$) and two intense reflections between 20 and 25°. On the contrary, PPMC X-ray spectra are appreciably different from those of PTeMC and PDMC. One can see that the XRD pattern of PPMC is characterized by strong reflections at 21.00°, 22.76° and by weaker reflections at 25.12° and 15.12°. Taking into account that the kind of pattern is strictly correlated to the crystal structure, a different packing should be hypothesized for poly(alkylene carbonate)s with the even or odd $\mathrm{Num_c}$.

As far as the poly(alkylene carbonate)s characterized merely by even $\mathrm{Num_c}$ are concerned, the increasing trend in crystallizing ability would be expected since polymers having longer aliphatic chains are more flexible, thereby crystallizing more readily. The same holds for the poly(alkylene carbonate)s bearing odd $\mathrm{Num_c}$. However, the odd–even fluctuation in the crystallization rate and T_m for poly(alkylene carbonate)s suggests that the chain flexibility is not the only factor. Other characteristics such as the crystal structure and the chain conformation might contribute to the odd–even effect [18]. The simplest way to interpret our results is to consider that to some extent, aliphatic poly(alkylene carbonate)s can be assimilated to polyethylene (PE) chains containing carbonate groups [18]. In this view, it would be expected for poly(alkylene carbonate)s having even $\mathrm{Num_c}$, that the carbonate groups act as the defects in the polyethylene chains resulting in the reduced crystallization ability. Thus for PTeMC, PHMC and PDMC,

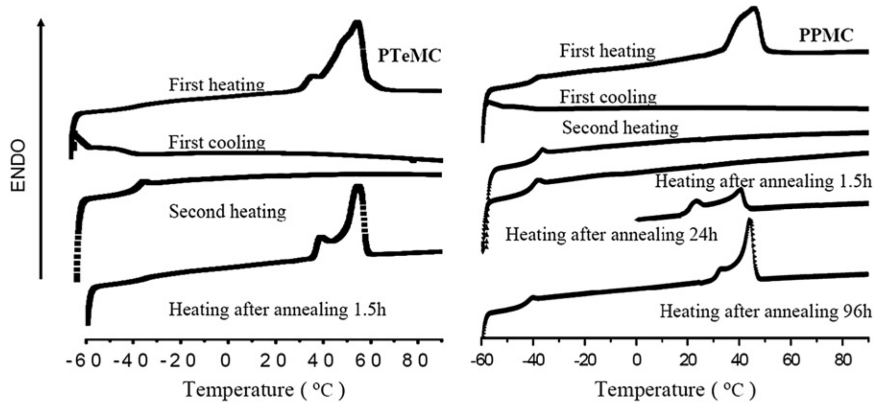


Fig. 5. DSC traces of PTeMC and PPMC. (Heating and cooling rates, 10 °C/min; the annealing course lasted 1.5 h).

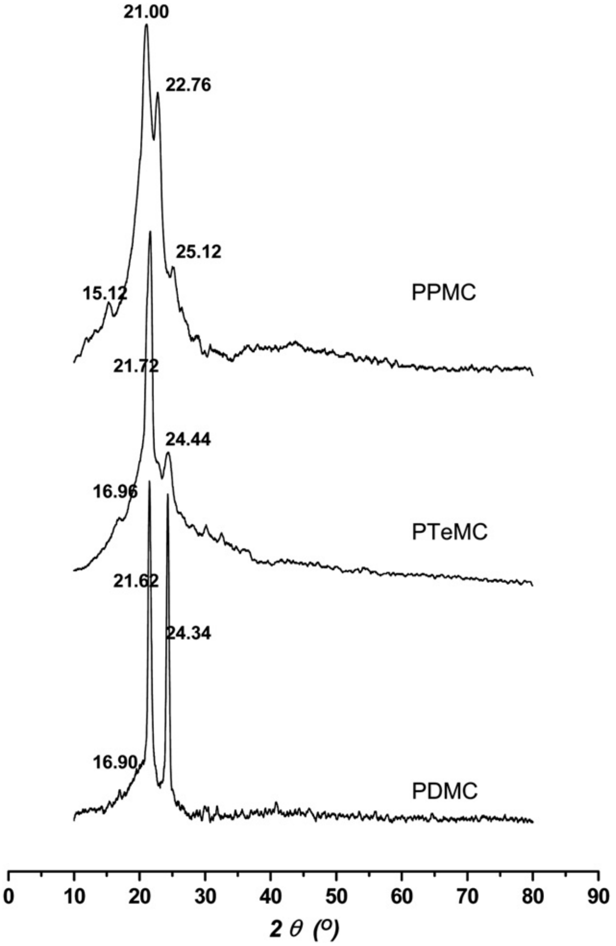


Fig. 6. WAXS patterns for PPMC, PTeMC and PDMC.

the polycarbonates having larger Num$_c$ behave more rapidly crystallizing because of its relatively lower concentration of carbonate groups. However for poly(alkylene carbonate) having odd Num$_c$, it can be mainly interpreted as a tendency of the polymer to adopt the crystalline conformation of PE since their structure deviates more from PE relative to the polycarbonates having even Num$_c$. Therefore, the retardation in PPMC crystallization, comparing to PTeMC which have one less CH_2 groups, is attributed to its chemical structure, and especially to its reduced symmetry caused by the pentylene units. For the same reason, it is not surprising that PTMC does not crystallize at all since its structure shows the largest deviation from PE.

4. Conclusion

$Sn(Oct)_2$ proved highly reactive to catalyze $(PMC)_2$ polymerization thereby providing poly(PMC) (PPMC) with the high molecular weights up to 1.7×10^5 g/mol and in high yields. The plot of M_n versus molar ratio of $(PMC)_2/Sn(Oct)_2$ appeared to fit the linear regression line with a correlation coefficient (r^2) of 0.995, indicating controllable feature of the polymerization. ^{1}H NMR analysis demonstrated that the PPMC prepared using $Sn(Oct)_2$ as catalyst contained –OH and octoate terminal groups, which suggested that $Sn(Oct)_2$ was more possible to play a role of initiator. The structure-thermal property relationship is discussed based on the comparative investigation on the crystallization behaviors of poly(alkylene carbonate)s with different number of CH_2 groups per repeat unit (Num$_c$), including PTMC (Num$_c$ = 3), PTeMC (Num$_c$ = 4), PPMC(Num$_c$ = 5), PHMC (Num$_c$ = 6), PDMC (Num$_c$ = 10). An interesting odd–even effect related to the Num$_c$ was first observed with regard to their crystallization rate and T_m. Poly(alkylene carbonate)s bearing even Num$_c$ were readily crystallizing relative to that bearing odd Num$_c$. A one-way decreasing trend of T_g was found when the Num$_c$ increased. DSC results indicate that longer annealing process would be beneficial for the perfection of PPMC's crystallinity.

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