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Synthesis of poly(ε-caprolactone)-*block*-poly(*n*-butyl acrylate) by combining ring-opening polymerization and atom transfer radical polymerization with $Ti[OCH_2CCl_3]_4$ as difunctional initiator: I. Kinetic study of $Ti[OCH_2CCl_3]_4$ initiated ring-opening polymerization of ε-caprolactone

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ABSTRACT

A new titanium alkoxide, $Ti[OCH_2CCl_3]_4$, designed to combine the ring-opening polymerization (ROP) of ε-caprolactone and atom transfer radical polymerization (ATRP) of *n*-butyl acrylate, was synthesized through the ester-exchange reaction of titanium *n*-propoxide and 2,2,2-trichloroethanol. The mechanism and kinetics of $Ti[OCH_2CCl_3]_4$ initiated bulk polymerization of ε-caprolactone were studied. The results demonstrate that the polymerization proceeds through the coordination–insertion mechanism and all the four alkoxide groups in $Ti[OCH_2CCl_3]_4$ share a similar activity in the initiation. The determined polymerization activation energy is 70 kJ/mol. The polymerization process can be well predicted by the obtained kinetic parameters. Furthermore, PCL synthesized with $Ti[OCH_2CCl_3]_4$ can be used as the macroinitiator in ATRP of *n*-butyl acrylate to synthesize poly(ε-caprolactone)-*block*-poly(*n*-butyl acrylate) (PCL-*b*-PBA) copolymer.

1. Introduction

ε-Caprolactone is one of the most widely studied monomers for the synthesis of degradable materials, and the most practical and convenient strategy to synthesize poly(ε-caprolactone) (PCL) is ROP initiated by metal alkoxides, such as aluminum [1–3], tin [4,5], magnesium [1,6], zinc [7,8], and titanium derivatives [1,9–13]. By carefully selecting the initiator systems, PCL functionalized with different end groups have been obtained, such as halogen groups [14,15], double bond [16–18], hydroxyl groups [19,20], and silane [21–23], which provides a wide range of possibilities for the synthesis of PCL-based copolymers with advanced structures such as block [24–26], star-shaped [27,28], comblike [29], brushlike [30], or cross-linked networks [31,32]. Meanwhile, ATRP has been proved to be efficient to synthesize polymer with desired macromolecular architectures [33–36]. Therefore, it is very interesting to combine ROP and ATRP to synthesize PCL-based copolymers with controlled length, composition, and architecture of polymer chains [37–40].

This work is a part of the subject concerning the synthesis of PCL-*b*-PBA by controlled polymerization. In this study, we present the synthesis and characterization of a new titanium alkoxide containing halogen groups, $Ti[OCH_2CCl_3]_4$, which was designed to be efficient as the difunctional initiator to combine ROP of ε-caprolactone and ATRP of *n*-butyl acrylate. Then the mechanism and kinetics of $Ti[OCH_2CCl_3]_4$ initiated ROP of ε-caprolactone were studied. The PCL synthesized with $Ti[OCH_2CCl_3]_4$ was used as a macroinitiator in the ATRP of *n*-butyl acrylate to synthesize PCL-*b*-PBA copolymers.

2. Experimental

2.1. Materials

Titanium *n*-propoxide (Aldrich, 98%), 2,2,2-trichloroethanol (Aldrich, ≥99%), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), and copper(I) chloride (Cu^ICl, Aldrich, ≥99%) were used as received. ε-Caprolactone (Solvay Company, 99%) and *n*-butyl acrylate (Aldrich, 98%) were distilled over calcium hydride.

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2.2. Characterization

Nuclear magnetic resonance (^{1}H NMR) spectra were recorded in Chloroform-D ($CDCl_3$) on a Bruker AVANCE 250 instrument working at 250 MHz, 25 °C. Chemical shift of proton is recorded with reference to internal tetramethylsilane (TMS).

Thermogravimetric analysis (TGA) was performed on SETARAM Thermoanalyzer G70. Approximately 70 mg sample was charged into a quartz crucible and analyzed under a constant flow of air (100 mL/min) over the range of 20–800 °C at a temperature increasing rate of 10 °C/min. The weight loss due to degradation was recorded as a function of temperature. As for titanium *n*-propoxide, it was PCL with low molecular weight that had been examined, because if only titanium *n*-propoxide was heated in TGA, it would evaporate during the heating.

The molecular weight and molecular weight polydispersity were determined by size exclusion chromatography (SEC). The detectors employed to measure the absolute molecular weights were a triple detector system containing refractive index detector (Waters 2414), viscometer detector (Wyatt Technology, ViscoStar) and a multi-angle laser light scattering detector (Wyatt Technology, miniDAWN TREOS) with the light wavelength of 690 nm. Four columns were used, Shodex KF-G, Shodex KF-801, Shodex KF-803, and Shodex KF-805. The eluent was tetrahydrofuran (THF) with a flow rate of 1 mL/min and the elution temperature is 30 °C. Absolute molecular weights were determined using ASTRA software (Wyatt Technology). The value of refractive index increments (d*n*/d*c*) was set as 0.075 mL/g for PCL-*b*-PBA copolymer in THF at 25 °C.

2.3. Synthesis and characterization of $Ti[OCH_2CCl_3]_4$

Titanium *n*-propoxide (5.00 g, 1.76×10^{-2} mol) and 2,2,2-trichloroethanol (15.77 g, 0.11 mol) were mixed in a round bottom flask and immersed in the oil bath thermostated at 70 °C for 1 h, the reaction was presented in Scheme 1. Then reduced pressure of 0.2 atm and 5×10^{-3} atm at 70 °C were applied to eliminate the produced *n*-propanol and the excess 2,2,2-trichloroethanol respectively on fractional distillation. In the end, a dark brown solid was obtained and used in the following experiments.

In order to characterize the structure of the product, both the nuclear magnetic resonance (^{1}H NMR) and the thermogravimetric analysis (TGA) have been applied. In the ^{1}H NMR spectrum, there is only one peak appearing at 4.2–5.5 ppm, no peak appears at 0.8–0.9 ppm and 3.0–3.1 ppm, which correspond to $-CH_3$ in titanium *n*-propoxide and –OH in 2,2,2-trichloroethanol, respectively. However, with ^{1}H NMR spectrum, there is no evidence to prove the inexistence of the oligomer that could be produced in the synthesis reaction [41,42]. Because the protons in the alkoxide groups of the oligomer give the same chemical shifts with those in $Ti[OCH_2CCl_3]_4$. Therefore, TGA was employed to prove the inexistence of oligomer. In the analysis of TGA, titanium alkoxides degrade into the volatiles of CO_2 and H_2O, and only titanium (IV) dioxide should be left. This is the foundation underlying the application of TGA to determine the chemical structure of $Ti[OCH_2CCl_3]_4$. By comparing the content of titanium (IV) oxide determined by TGA and the theoretical value, it is possible to evaluate the structure of $Ti[OCH_2CCl_3]_4$. The TGA curves are shown in Fig. 1. For the TGA results of titanium *n*-propoxide, there is 1.2% error between the theoretical and experimental value, which means that the TGA method is applicable to evaluate the chemical structure of titanium *n*-propoxide, if taken the purity of titanium *n*-propoxide into account. Combining the information derived from ^{1}H NMR and TGA (there is 1.9% error between theoretical and experimental value), the chemical structure of synthesized $Ti[OCH_2CCl_3]_4$ can be confirmed: it is the titanium alkoxide with four trichloroethanol arms, not the oligomer formed by $Ti[OCH_2CCl_3]_4$ molecules.

2.4. Bulk polymerization of ε-caprolactone

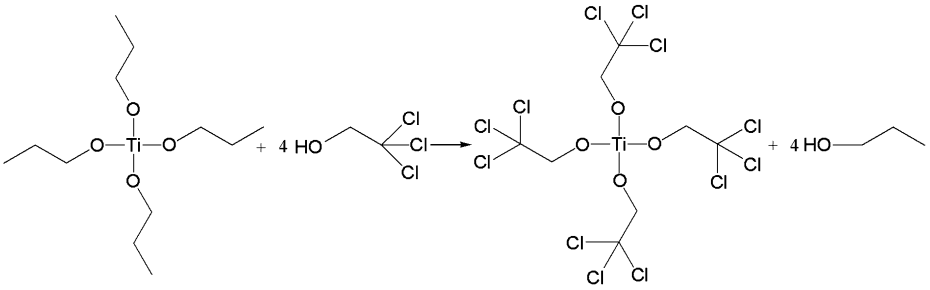
The bulk polymerization of ε-caprolactone was described with an following example: ε-caprolactone (50 g, 0.44 mol) and $Ti[OCH_2CCl_3]_4$ (0.70 g, 1.10×10^{-3} mol) were charged into a dry flask at room temperature, and stirred for 15 min. Then 2 g of the mixture were injected into the tubes sealed with silicon caps, and immersed into an oil bath thermostated at 90 °C. At different time, the tubes were removed from the oil bath and immersed into liquid nitrogen immediately to stop the polymerization. The samples in the tubes were examined directly on a Bruker AVANCE 250 nuclear magnetic resonance instrument to follow the polymerization process. For the other experiments, only *DPn*(*set*) and the polymerization temperature were changed. *DPn*(*set*) is the degree of polymerization predetermined according to equation (1).

$$DPn(set) = \frac{w_{CL}/M_{CL}}{4 \times w_{Ti}/M_{Ti}} \quad (1)$$

where w_{CL} and M_{CL} are the mass used in the experiment and the molecular weight of ε-caprolactone, respectively; w_{Ti} and M_{Ti} are the mass used in the experiment and the molecular weight of $Ti[OCH_2CCl_3]_4$, respectively.

2.5. Synthesis of PCL-b-PBA by combining ROP of ε-caprolactone and ATRP of n-butyl acrylate

To synthesize PCL-*b*-PBA by combining ROP of ε-caprolactone and ATRP of *n*-butyl acrylate, ε-caprolactone (4.45 g, 3.90×10^{-2} mol) and $Ti[OCH_2CCl_3]_4$ (0.25 g, 3.90×10^{-4} mol) were charged into a dry Schlenk flask equipped with a magnetic stirring



Scheme 1. Synthesis of $Ti[OCH_2CCl_3]_4$.

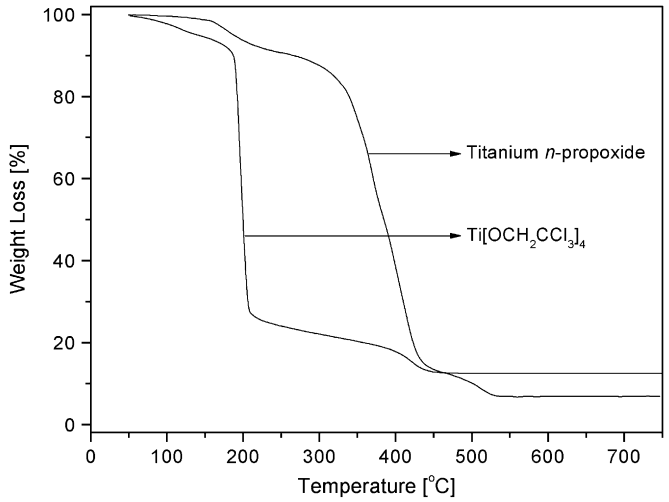


Fig. 1. TGA curves of $Ti[OCH_2CCl_3]_4$ and titanium *n*-propoxide (contained in PCL).

bar and sealed with a rubber septum at room temperature. After the initiator had been dissolved, the flask was immersed in an oil bath heated at 80 °C for 12 h. Then the flask was cooled to the room temperature and *n*-butyl acrylate (5.00 g, 3.90×10^{-2} mol) was charged. After the PCL had been dissolved, $Cu^{I}Cl$ (0.15 g, 1.56×10^{-3} mol) and PMDETA (0.41 g, 2.34×10^{-3} mol) were charged. The resulting clear solution was degassed by three freeze-pump-thaw cycles and back filled with nitrogen. Then the flask was immersed in an oil bath thermostated at 80 °C for 12 h. In this study, the ratio of ε-caprolactone to *n*-butyl acrylate was kept as 1:1(mol) for all the polymerization; therefore, the PCL and PBA segments in the synthesized PCL-*b*-PBA copolymers have the same set polymerization degree, that is, $DPn(set,PCL) = DPn(set,PBA)$. The synthesis reaction of PCL-*b*-PBA copolymer was shown by Scheme 2.

3. Results and discussion

3.1. Mechanism of $Ti[OCH_2CCl_3]_4$ initiated ROP of ε-caprolactone

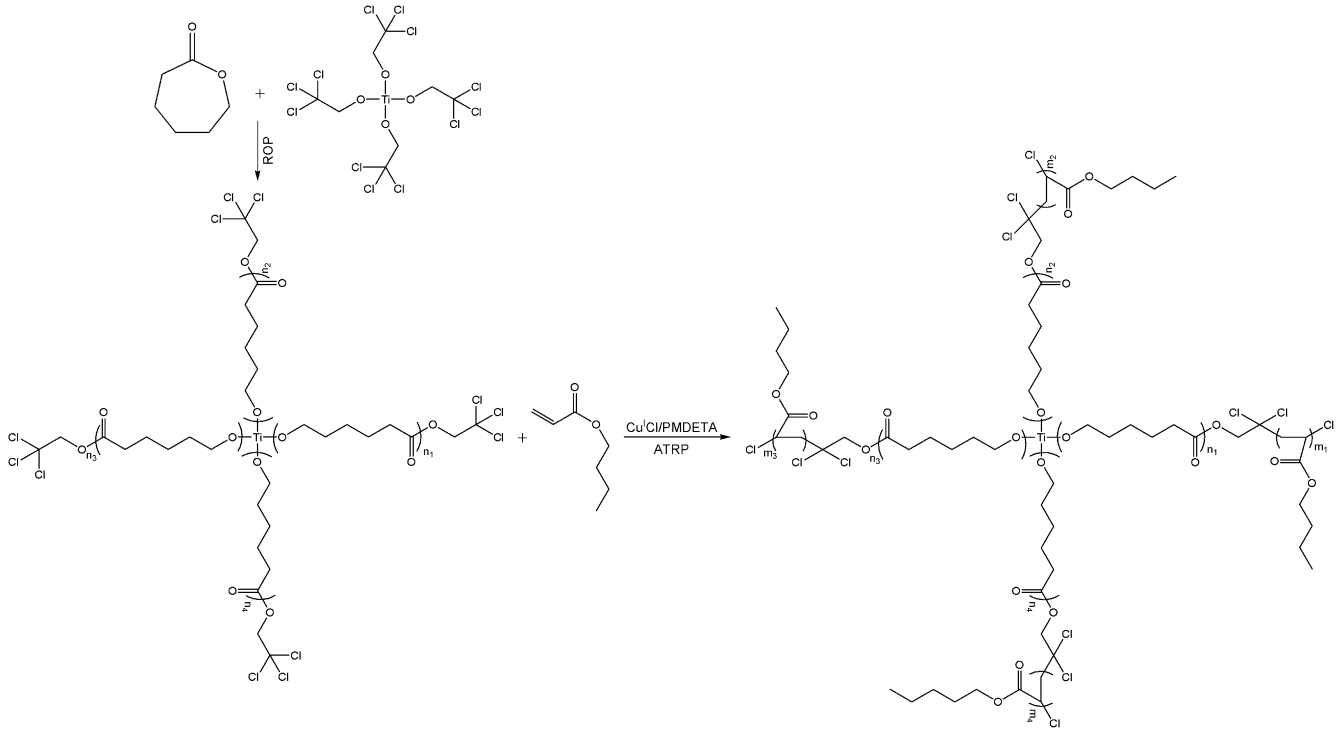
ROP of ε-caprolactone initiated by alkoxides and organometallic derivatives of transition metals of groups III and IV, such as zinc, tin, germanium, aluminum and titanium, proceed through a "coordination–insertion" mechanism [43]. For $Ti[OCH_2CCl_3]_4$ initiated ROP of ε-caprolactone, the mechanism should be the same with other titanium derivatives. The predicted mechanism of $Ti[OCH_2CCl_3]_4$ initiated polymerization of ε-caprolactone is shown in Scheme 3. In the polymerization, ε-caprolactone monomer inserts into the "Ti–O" bond of $Ti[OCH_2CCl_3]_4$. The acyl-oxygen bond of ε-caprolactone is cleaved in such a way that the growing chain remains attached to titanium through an alkoxide bond, and the alkoxide group in $Ti[OCH_2CCl_3]_4$ is transferred to the end of PCL chain. Furthermore, it is well known that one of the most convictive character of living ROP is that the molecular weight of polymer is proportional to monomer conversion in the process of polymerization. To evaluate the mechanism of $Ti[OCH_2CCl_3]_4$ initiated ROP of ε-caprolactone in our experiments, the average degree of polymerization determined from ^{1}H NMR spectra, $DPn(NMR)$, corresponding to the average number of ε-caprolactone unit per arm of PCL, was compared with the theoretical value, $DPn(theo)$, at different conversion of ε-caprolactone.

$DPn(theo)$ corresponding to different monomer conversion is calculated by the following equation.

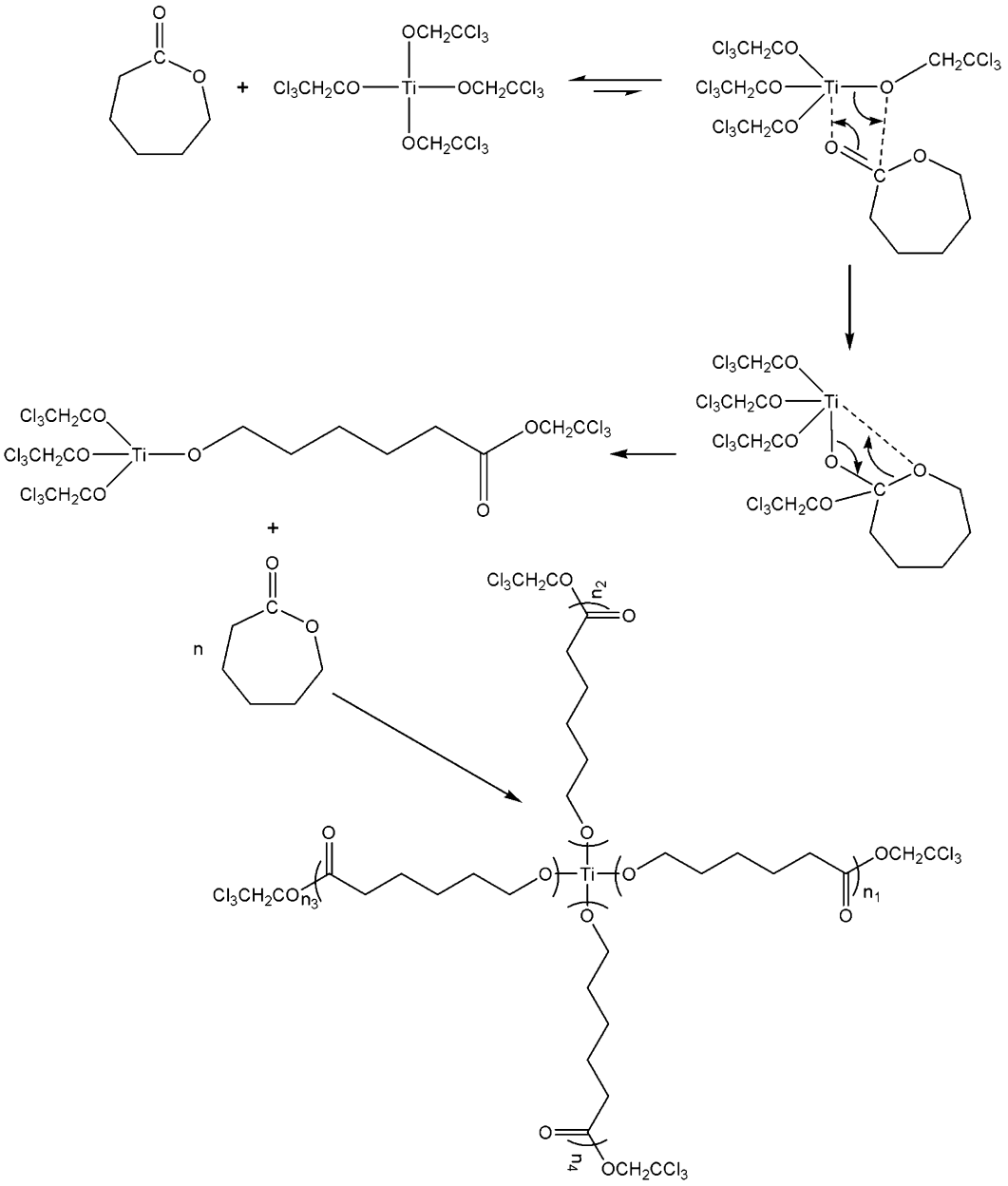
$$DPn(theo) = \frac{M_0}{4 \times I_0}\alpha = DPn(set)\alpha \quad (2)$$

where α is the conversion of ε-caprolactone, M_0 and I_0 are the initial molar quantity of ε-caprolactone and $Ti[OCH_2CCl_3]_4$, respectively.

Fig. 2 shows the ^{1}H NMR spectra of the samples collected during the $Ti[OCH_2CCl_3]_4$ initiated polymerization of ε-caprolactone ($DPn(set) = 100$, 90 °C). For the synthesized PCL, protons in the end



Scheme 2. Synthesis of PCL-*b*-PBA copolymer.



Scheme 3. Mechanism of $Ti[OCH_2CCl_3]_4$ initiated polymerization of ε-caprolactone.

group share the same chemical shifts just as they are in $Ti[OCH_2CCl_3]_4$. Corresponding to $-^{\varepsilon'}CH_2$ in ε-caprolactone, $-^{\varepsilon}CH_2$ moves to 2.2–2.4 ppm, which provides the possibility to determine the conversion of ε-caprolactone by comparing the integral of $-^{\varepsilon}CH_2$ with that of $-^{\varepsilon'}CH_2$, as shown in equation (3). And using $-^{a}CH_2$ in the end group and $-^{\varepsilon}CH_2$ in PCL, *DPn*(*NMR*) can be determined according to equation (4).

$$\alpha = \frac{I_{(\varepsilon)}}{I_{(\varepsilon')} + I_{(\varepsilon)}} 100\% \tag{3}$$

where $I_{(\varepsilon)}$ and $I_{(\varepsilon')}$ are the integral of peak (ε) and peak (ε′), respectively.

$$DPn(NMR) = \frac{I_{(\varepsilon)}}{I_{(a)}} \tag{4}$$

where $I_{(a)}$ is the integral of peak (a).

The comparison between *DPn*(*NMR*) and *DPn*(*theo*) of the bulk polymerization of ε-caprolactone (*DPn*(*set*) = 100, 90 °C) is shown in Fig. 3. It should be noted that in the polymerization with *DPn*(*set*) = 100, the concentration of $Ti[OCH_2CCl_3]_4$ is very low, the integral of peak (a) in $-OCH_2CCl_3$ end group of PCL is very small, which can introduce a serious error when using peak (a) to determine the *DPn*(*NMR*). Therefore, taken into the error introduced by peak (a), the conclusion that *DPn*(*NMR*) is linear to monomer conversion in the process of $Ti[OCH_2CCl_3]_4$ initiated polymerization of ε-caprolactone is still acceptable. However, no information concerning the dependence of molecular weight polydispersity on the conversion of ε-caprolactone can be derived from ^1H NMR in this study, therefore it is difficult to conclude that the $Ti[OCH_2CCl_3]_4$ initiated ROP of ε-caprolactone is exactly a living polymerization.

In order to evaluate the initiating activity of each alkoxide arm of $Ti[OCH_2CCl_3]_4$, N_a, the average number of active alkoxide arm per

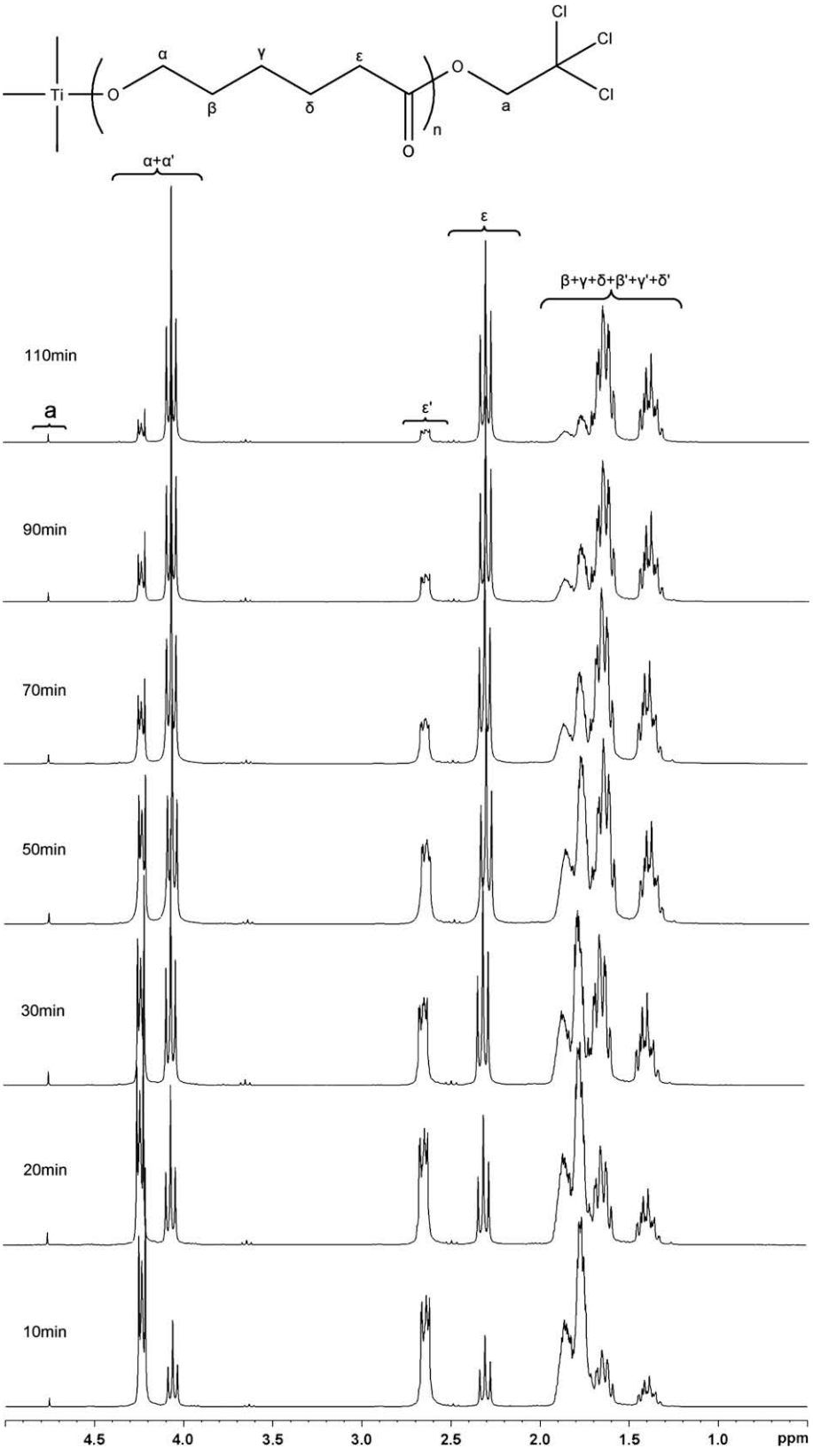


Fig. 2. ^{1}H NMR spectra of samples collected from $Ti[OCH_2CCl_3]_4$ initiated polymerization of ε-caprolactone ($DPn(set) = 100$, 90 °C).

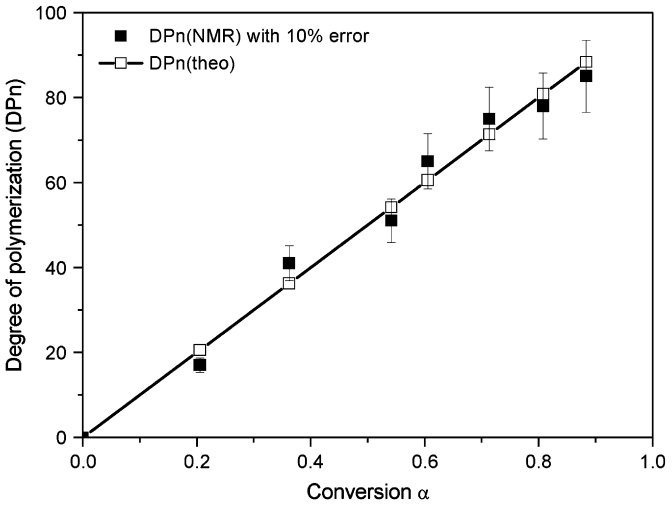


Fig. 3. Comparison of *DPn*(*NMR*) and *DPn*(*theo*) at different conversion for the bulk polymerization of ε-caprolactone (*DPn*(*set*) = 100, 90 °C).

$Ti[OCH_2CCl_3]_4$ was determined by ^1H NMR spectra of PCL according to equation (5). If all the four alkoxide arms in $Ti[OCH_2CCl_3]_4$ were active and sharing a similar activity on initiating the ROP of ε-caprolactone, each PCL chain theoretically has the same chain length in the process of polymerization, and the degree of polymerization is also proportional to the conversion of ε-caprolactone. Under that condition, N_a should be equal to 4, like that of titanium *n*-propoxide [1,44].

$$N_a = \frac{M_0/I_0}{DPn(NMR)}\alpha = \frac{4DPn(set)}{DPn(NMR)}\alpha \tag{5}$$

According to the *DPn*(*NMR*) and *DPn*(*theo*) data in Fig. 3, N_a is close to 4, which demonstrates that all alkoxide arms are active and share a similar activity to initiate ε-caprolactone from the beginning of polymerization.

3.2. Kinetics of $Ti[OCH_2CCl_3]_4$ initiated ROP of ε-caprolactone

Titanium alkoxide initiated bulk ring-opening polymerization of ε-caprolactone is first order in monomer; therefore the conversion of ε-caprolactone and the polymerization rate can be expressed by equations (6) and (7), respectively.

$$\alpha = \frac{[M]_0 - [M]_t}{[M]_0} = 1 - \frac{[M]_t}{[M]_0} \tag{6}$$

$$\frac{-d[M]_t}{dt} = K(T)[M]_t \tag{7}$$

where $[M]_0$ and $[M]_t$ are the monomer concentration at the beginning and up to time *t*, respectively, $K(T)$ is the apparent polymerization rate constant, defined by equation (8).

$$K(T) = k_0 e^{-\frac{E_a}{RT}}[I]^m \tag{8}$$

where E_a is the activation energy, k_0 is a constant, $[I]$ is the initiator concentration, m is the reaction order of initiator, T is the Kelvin temperature, and R is the universal gas constant.

Combining equations (6) and (7), then integrate, the following equation can be obtained.

$$-\ln(1-\alpha) = K(T)t \tag{9}$$

Obviously, $K(T)$ can be obtained from the slope of the plot of $-\ln(1-\alpha)$ vs. *t*.

In this study, the kinetics of the bulk polymerization of ε-caprolactone was studied by ^1H NMR, and the spectra of samples collected from the polymerization (*DPn*(*set*) = 100, 90 °C) are presented as an example in Fig. 2.

The plots of $-\ln(1-\alpha)$ vs. *t* for two different *DPn*(*set*) at five temperatures are presented in Fig. 4, and the determined $K(T)$ is summarized in Table 1.

According to equation (8), the activation energy E_a can be obtained from the slope of the plot of $\ln[K(T)]$ vs. $1/T$, as shown in Fig. 5. The determined activation energy E_a is 70 kJ/mol. Furthermore, from the plot of $\ln[K(T)]$ vs. $1/T$, for the polymerization of *DPn*(*set*) = 100 and 200, the apparent reaction rate constant $K(T)$ as a function of temperature can be given by the following equation.

$$K(T)_{DPn(set)=100} = 3.47 \times 10^6 \times \exp\left(-\frac{8341}{T}\right) \tag{10}$$

$$K(T)_{DPn(set)=200} = 3.09 \times 10^5 \times \exp\left(-\frac{8291}{T}\right) \tag{11}$$

Applying the apparent reaction rate constant $K(T)$ derived by equation (10) or 11 into equation (9), for the polymerization with *DPn*(*set*) = 50 or 100, at a certain temperature, the conversion of ε-caprolactone can be predicted, and the polymerization process can be described with the kinetic parameters obtained.

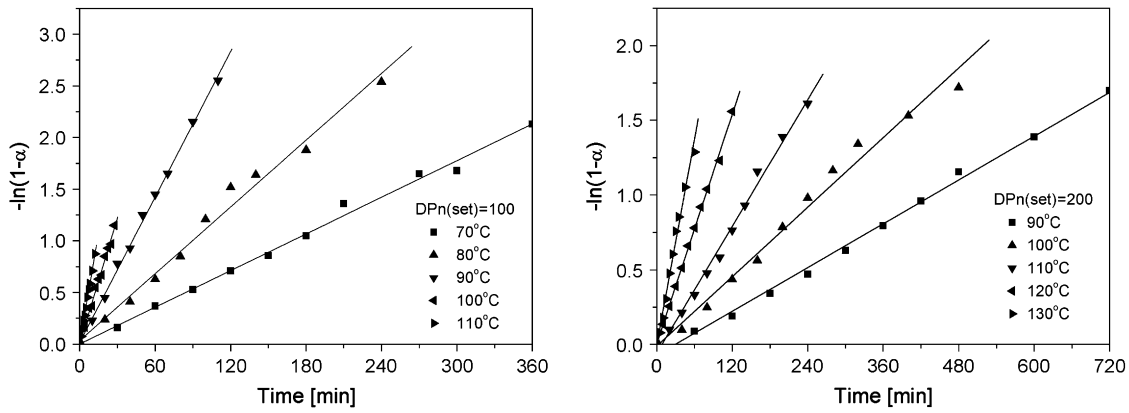


Fig. 4. $-\ln(1-\alpha)$ as a function of time *t* at different temperatures for the polymerization with *DPn*(*set*) = 100 and 200.

Table 1
The apparent reaction rate constant $K(T)$ determined by ^{1}H NMR.

T (°C)	$K(T)_{DPn(set)=100}$ ($s^{-1} \times 10^{-4}$)	T (°C)	$K(T)_{DPn(set)=200}$ ($s^{-1} \times 10^{-4}$)
70	0.99	90	0.41
80	1.80	100	0.65
90	3.91	110	1.18
100	6.74	120	2.13
110	12.1	130	3.82

3.3. Synthesis of PCL-b-PBA copolymer by combining ROP of ε-caprolactone and ATRP of n-butyl acrylate

PCL synthesized with $Ti[OCH_2CCl_3]_4$ has been functionalized by trichloroethanol end groups, which can be used as the initiator in ATRP. Although there are three chloride atoms in each arm of the initiator, it is suggested in literature that only one chloride atom is viable for the initiation [45–48].

The ^{1}H NMR spectra of $Ti[OCH_2CCl_3]_4$ initiated PCL and PBA are presented in Fig. 6. For $Ti[OCH_2CCl_3]_4$ synthesized PBA ($DPn(set) = 25$), $-^aCH_2$ overlaps with $-^CCH_2$. The $-CH_2$ (linked to $-CCl_2$) in the first *n*-butyl acrylate repeating unit and –CH (linked to –CCl) in the last *n*-butyl acrylate repeating unit appear at around 2 ppm and 4.2 ppm, respectively, and they overlap with other peaks. Comparing the spectra of PCL and PBA in Fig. 6, it shows that for PBA all the protons appear at the same chemical shifts with those protons from PCL except for $-^FCH_3$. In the following, $-^FCH_3$ is used to determine the composition in PCL-*b*-PBA copolymer.

^{1}H NMR spectra of PCL-*b*-PBA copolymer with different molecular weight are shown in Fig. 7. In Fig. 7, the signals for the protons of CH_2═CH in *n*-butyl acrylate monomer totally disappear from the spectrum of PCL-*b*-PBA copolymer, this observation indicates that the conversion of *n*-butyl acrylate is complete. In the following calculation, it was taken as 100%. Using the protons in the segments of PCL and PBA, the molar fraction of PCL and PBA segments in PCL-*b*-PBA copolymer can be determined according to equation (12).

$$\frac{\mathrm{PCL}}{\mathrm{PBA}} = \frac{\left[I_{(a+\alpha+C)} - 2I_{(F)}/3\right]/2}{I_{(F)}/3} \tag{12}$$

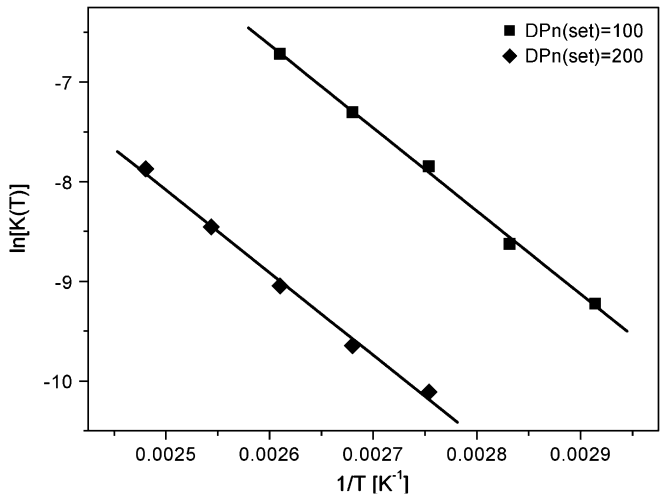


Fig. 5. ln[$K(T)$] as a function of $1/T$.

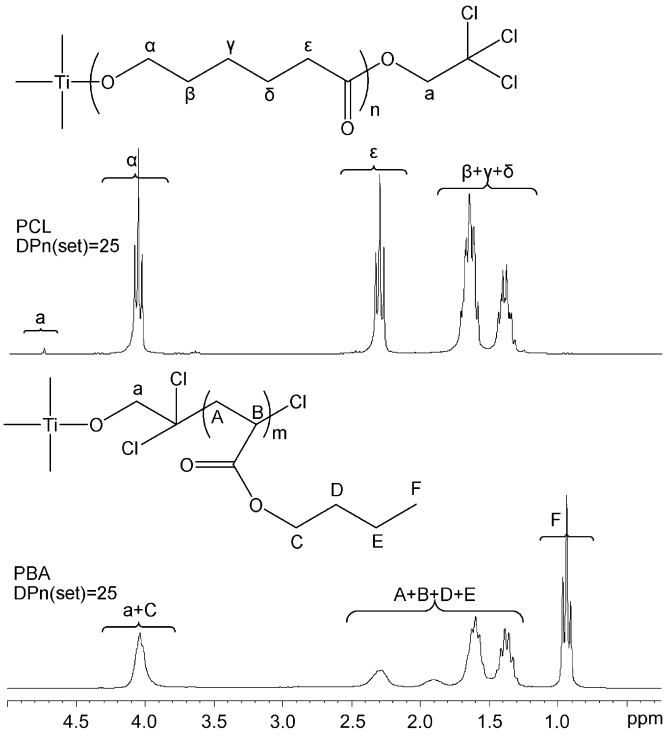


Fig. 6. ^{1}H NMR spectra of PCL and PBA synthesized with $Ti[OCH_2CCl_3]_4$.

where $I_{(a+\alpha+C)}$ and $I_{(F)}$ are the integral of peaks (a + α + C) and peaks (F), respectively.

Table 2 presents the ^{1}H NMR determined molar fraction of PCL and PBA segments in PCL-*b*-PBA copolymer. The results

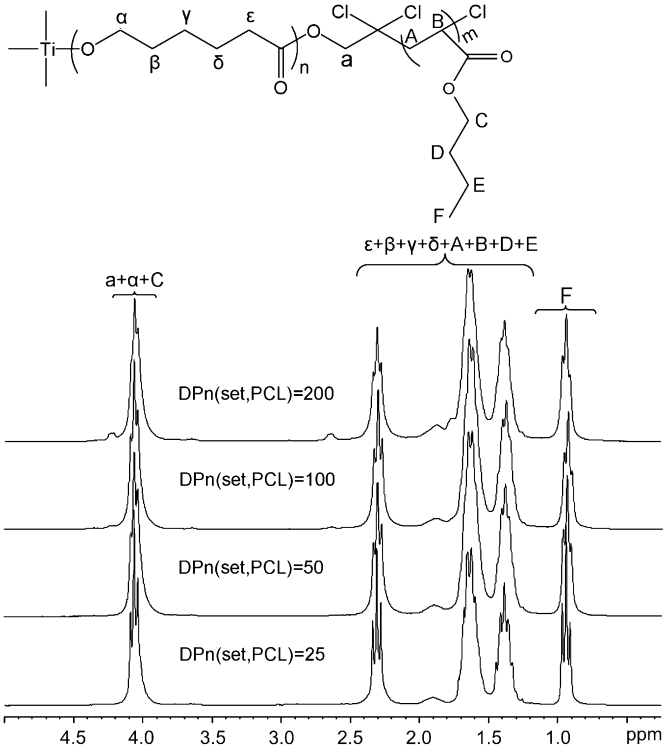


Fig. 7. ^{1}H NMR spectra of PCL-*b*-PBA copolymer with different molecular weight.

Table 2
Molar fraction of PCL and PBA segments in PCL-*b*-PBA copolymer.

DPn(*set*,*PCL*)	CL/BA (mol)	Conversion (CL,wt%)	Conversion (BA,wt%)
25	0.95/1	98	100
50	0.95/1	98	100
100	0.93/1	97	100
200	0.91/1	94	100

demonstrate that the molar fraction of PCL to PBA segment in the synthesized PCL-*b*-PBA copolymer decreases from 0.95 to 0.91 with the set polymerization degree of PCL segment increased from 25 to 200, this results stem from the decreasing of ε-caprolactone conversion in the polymerization.

Fig. 8 shows the SEC traces of PCL-*b*-PBA copolymer with different molecular weight. For each PCL-*b*-PBA copolymer, the SEC trace shows only one single peak and the peak shifts to shorter elution time with increasing of the molecular weight.

The determined molecular weight is summarized in Table 3, and the theoretical molecular weight $M_n(theo)$ is calculated by equation (13).

$$M_n(theo) = DPn(set,PCL)M(\mathrm{CL}) + DPn(set,PBA)M(\mathrm{BA}) + M(-\mathrm{OCH_2CCl_3}) \quad (13)$$

where *DPn*(*set*,*PCL*) and *DPn*(*set*,*PBA*) are the set polymerization degree of PCL and PBA, respectively; *M*(CL), *M*(BA) and *M*(–OCH_2CCl_3) are the molecular weight of ε-caprolactone, *n*-butyl acrylate and –OCH_2CCl_3 part, respectively.

The results in Table 3 demonstrate that there is a difference of around 30% between the theoretical and SEC obtained molecular weight. When SEC is used, the molecular mass obtained depends on the hydrodynamic volume, which is different between the copolymer and homopolymer; in our case, the refractive index increments (d*n*/d*c*) used is 0.075 mL/g, which is the value for PCL in THF at 25 °C. This factor contributes to the disparity between the theoretical and SEC obtained molecular weight. Furthermore, the results demonstrate that with PCL macroinitiator, at high monomer conversion, the ATRP synthesized PCL-*b*-PBA copolymer has a higher molecular weight polydispersity index compared with that from a perfect controlled ATRP.

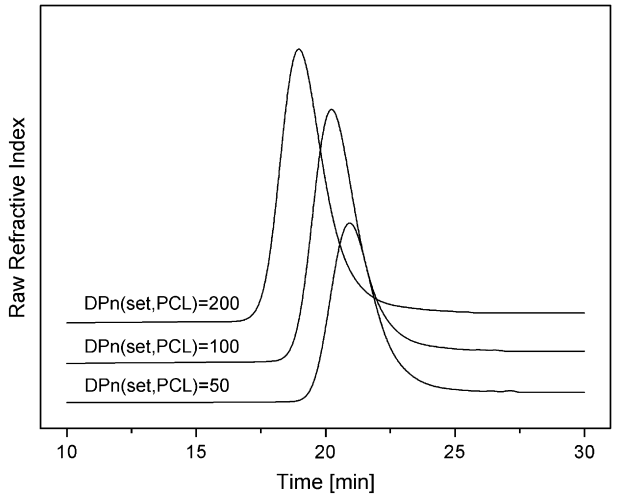


Fig. 8. SEC traces of PCL-*b*-PBA copolymer with different molecular weight.

Table 3
SEC determined molecular weight of PCL-*b*-PBA copolymer.

DPn(*set*,*PCL*)	$M_n(theo)$ (g/mol)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
50	12,300	15,100	10,700	1.41
100	24,400	28,500	20,800	1.37
200	48,600	63,200	51,700	1.22

4. Conclusions

$Ti[OCH_2CCl_3]_4$, a new titanium alkoxide for the ring-opening polymerization of ε-caprolactone and atom transfer radical polymerization of *n*-butyl acrylate, was synthesized and characterized. The mechanism and kinetics of $Ti[OCH_2CCl_3]_4$ initiated bulk polymerization of ε-caprolactone were investigated, and the results demonstrate that $Ti[OCH_2CCl_3]_4$ initiated polymerization of ε-caprolactone proceeds according to the coordination–insertion polymerization mechanism, and all the four alkoxide arms in $Ti[OCH_2CCl_3]_4$ are active and share a similar activity on initiating the polymerization of ε-caprolactone. The polymerization activation energy is 70 kJ/mol. Furthermore, $Ti[OCH_2CCl_3]_4$ synthesized PCL as a macroinitiator, Cu^ICl/PMDETA complexes as catalyst, poly(ε-caprolactone)-*block*-poly(*n*-butyl acrylate) has been successfully synthesized via ATRP of *n*-butyl acrylate.

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