

Preparation of Unsaturated Poly(ϵ -caprolactone) with a New Titanium Alkoxide Initiator

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ABSTRACT: Titanium alkoxides are widely used in the ring-opening polymerization of ϵ -caprolactone. In this study, functional poly(ϵ -caprolactone) was synthesized with a new titanium initiator by a two-step procedure: First, the titanium initiator, with an unsaturated group, was prepared by a classical organic reaction between 2-hydroxyethylmethacrylate or 2-allyloxyethanol with titanium tetrapropoxide; then, we initiated the polymerization of the ϵ -caprolactone monomer in a glass reactor or twin-screw extruder. By means of NMR spectroscopy, the structures of the initiators and polymers were determined.

When 2-hydroxyethylmethacrylate was used, there was a side reaction (transesterification) during the preparation of the initiator, and so it was impossible to obtain the expected product. With 2-allyloxyethanol, the designed titanium initiator was synthesized with high purity, and the allyl moiety remained intact after the polymerization of ϵ -caprolactone. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1772–1780, 2008

Key words: metal-organic catalysts/organometallic; reactive extrusion; ring-opening polymerization

INTRODUCTION

Research focusing on poly(ϵ -caprolactone) (PCL) is a very active and expanding area of polymer science because of the polymer's availability, variable biodegradability, good compatibility, and good mechanical properties. PCL and PCL-based blends and copolymers are widely used in biomedical and pharmaceutical applications.

As is well known, initiator-assisted ring-opening polymerization (ROP)^{1–7} is the most efficient way to produce high-molar-mass polymers in a controllable manner. Covalent metal alkoxides based on aluminum or zinc have proven to be effective initiators for the polymerization of ϵ -caprolactone (CL). The polymerization has been shown to proceed via a coordination–insertion mechanism, which involves the successive insertion of the monomer into the metal–O bond, which leads to the formation of an ester group at one end of the chain and an alkoxide group at the other end.

There are several ways to prepare PCL with an unsaturated group. One method is to functionalize a prepared hydroxyl-terminated PCL with maleic anhydride, fumaric acid, methacrylic anhydride,^{8–11} or

methacryloyl chloride,^{12,13} the other is to initiate the polymerization of CL with a functional alcohol with an initiator to obtain the appropriate polymer.^{14,15} For example, aluminum alkoxides [Al(OCH₂CH₂X)₃] carrying a functional group [e.g., X=Br, CH₂CH=CH₂, OCOC(Me)=CH₂,...] have been used as efficient initiators for the ROP of lactones.^{16,17} The hydrolysis of the active aluminum alkoxide bond leads to the formation of an asymmetric telechelic polyester; the end groups would be X and OH, respectively.

In this study, the ROP of CL was carried out with a new kind of initiator that was synthesized by the chemical modification of titanium tetrapropoxide [Ti(OPr)₄] because titanium alkoxides are one kind of the initiator for the ROP of CL.¹⁸ The modification depends on the group change reactions.^{19–22} The aim of this study was to prepare and characterize functional polycaprolactone (PCL) with a new initiator in a glass reactor and by reactive extrusion. The first part of this study was to examine the preparation of new titanium alkoxides carrying double-bond groups. The initiator was prepared by an efficient one-step process (Scheme 1). At first, 2-hydroxyethylmethacrylate (HEMA), which has been used as a coinitiator in some studies,^{14,16,23–26} was used as a reagent, but we found that the chemical modification reaction was impossible to control, and the characterizations proven there were some transesterification reactions. When 2-allyloxyethanol (AEOH) was

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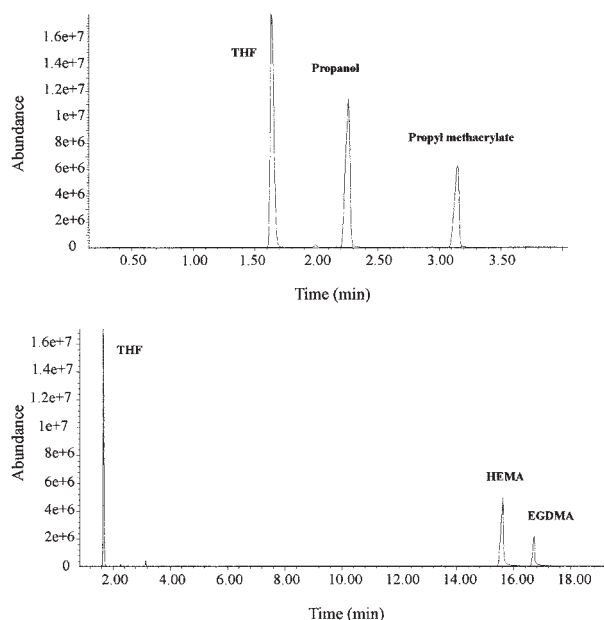


Figure 2 GC-MS spectra of the volatile fraction of the reaction of $\text{Ti}(\text{OPr})_4$ and HEMA at different times.

mL/min. The sample was kept at this temperature for 1 h.

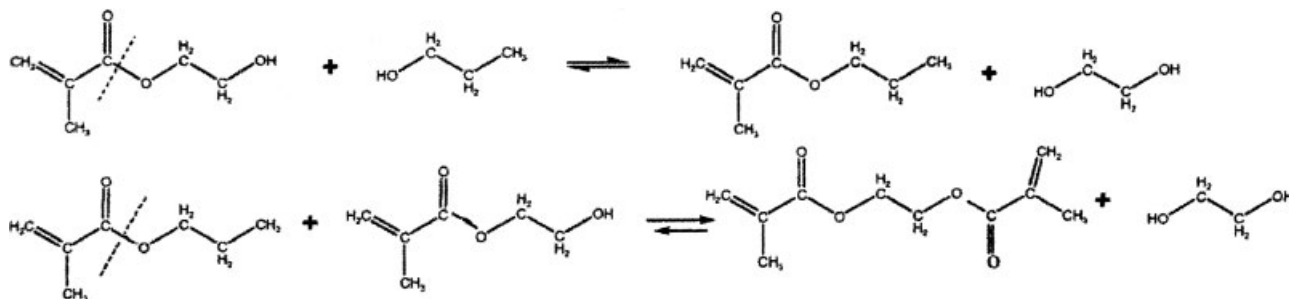
Size exclusion chromatography (SEC) was performed with a Waters 515 device (Guyancourt, France) equipped with a double detector (UV and differential refractometer). Waters columns HR1, HR3, and HR4, with separation performances ranging from 10^2 to 6.10^5 g/mol by the weight-average molar mass of polystyrene (PS), were used. PCL was first hydrolyzed and vacuum-dried; then, solutions of PCL were prepared in THF and filtered on a filter plate (pore size = $0.45 \mu\text{m}$) before injection.

THF was used as eluent at a flow rate of 1 mL/min. PCL or PS standards were used for the calibration curve.

RESULTS AND DISCUSSION

Modification from HEMA

The initiator was prepared according to the description in Scheme 1. The analysis by GC-MS of the



Scheme 2 Reactions with HEMA.

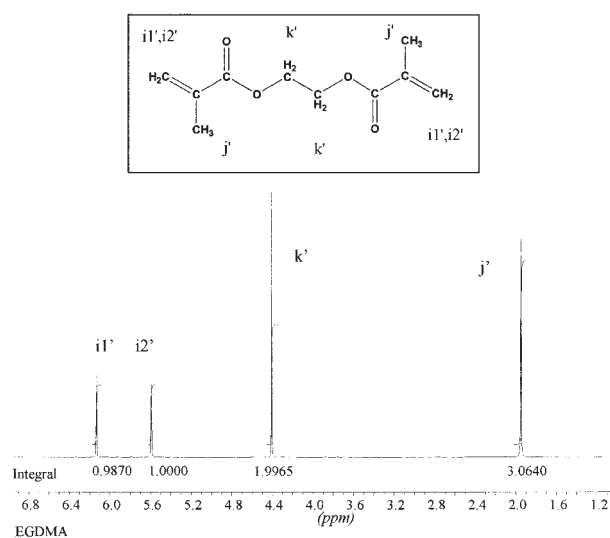


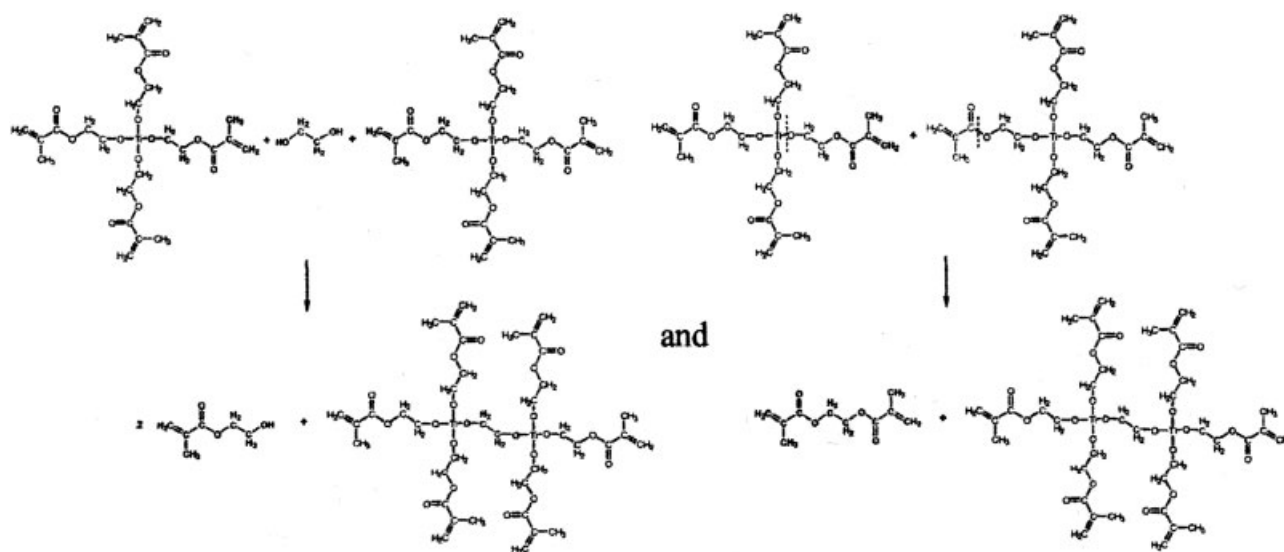
Figure 3 NMR spectrum of EGDMA.

products extracted showed the presence of propanol and the excess of HEMA. However, the GC-MS spectrum showed the presence of propyl methacrylate (Fig. 2) and ethylene glycol dimethacrylate (EGDMA). The ^1H -NMR spectrum of EGDMA is shown in Figure 3.

These side products could be assigned to the esterification reactions. Indeed, with organic titanium compounds, some transesterification reactions were carried out with HEMA ester groups, and possible reactions were proposed to explain the appearance of propyl methacrylate and EGDMA in our experiment (Scheme 2).

Ethylene glycol ($196\text{--}198^\circ\text{C}$, 1 atm) has a high boiling point, so it remained in the flask as an alcohol to continue the ester exchange reaction. Two Ti segments were connected together via an unstable Ti-O bond, as shown in Scheme 3. So, the viscosity of the new initiator in the reactor increased with the reaction time. The ^1H -NMR results of two samples at different reaction times are shown in Figure 4. The assignments are given in Table I.

We did not detect in any case unreacted titanium propoxide reagent because the different signals (CH_3



Scheme 3 Ester exchange reactions with alkoxide titanium.

at 0.935 ppm and CH₂ at 1.585 and 3.59 ppm) disappeared.

The absence of Ti(OPr)₄ indicated that the reaction shown in Scheme 1 was carried out. Propanol, as one of the reaction products with a very low boiling point, was distilled *in vacuo* to improve the yield of the reaction. So, the ¹H-NMR spectra (Fig. 4) could be divided into three parts: part A was the signal at

1.948 ppm corresponding to CH₃ group of the initiator, and part B consisted of the signals at 6.15 and 5.59 ppm, which were ascribed to the unsaturated group. The intensity ratio of part A to part B (*S_A/S_B*) was 3 : 2, which indicated that the segment of CH₂=CH(CH₃)CO— remained unchanged in the reactions and the double bond remained stable (otherwise, *S_A/S_B* would have been higher than 3 : 2). These

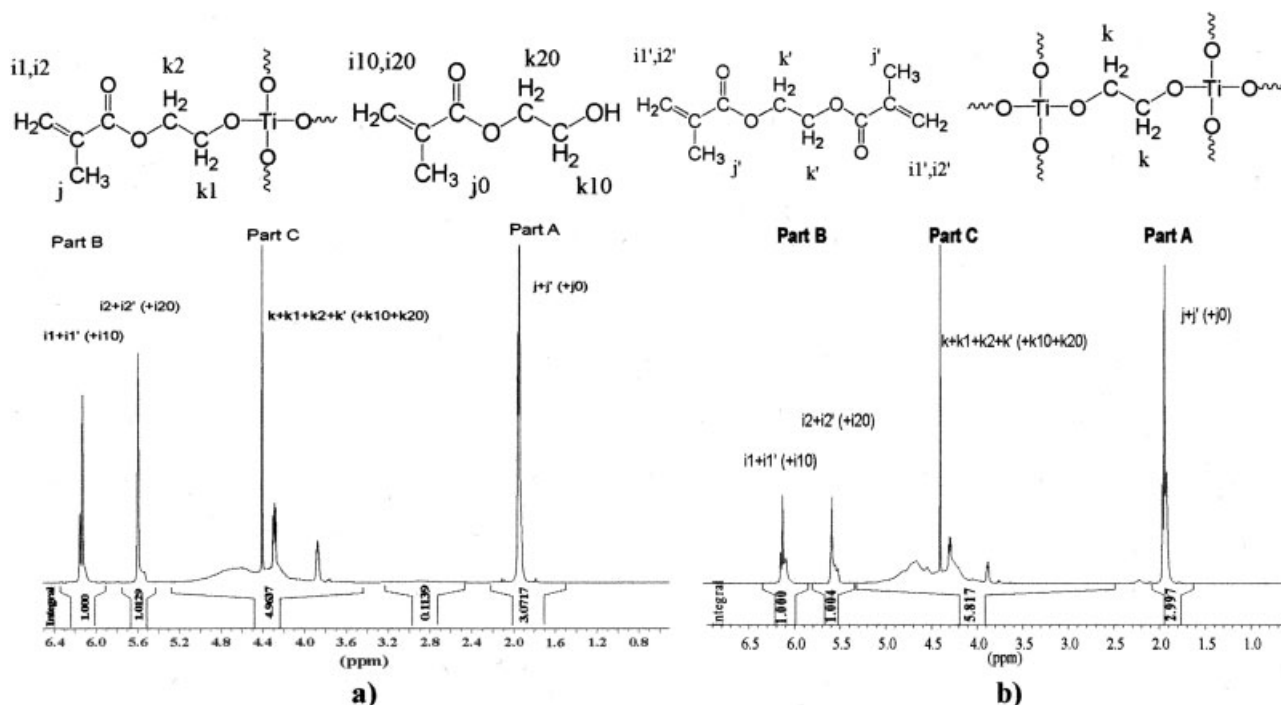
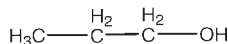
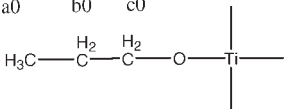
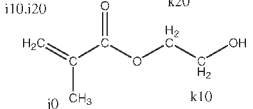
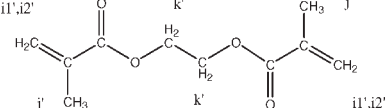
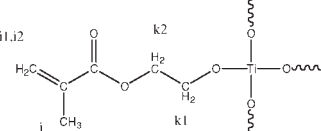
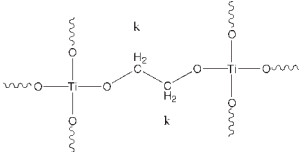


Figure 4 ¹H-NMR spectra of the product of Ti(OPr)₄ modified by HEMA for (a) 1 and (b) 2 h at a pressure of 0.2 mbar and a temperature of 70°C.

TABLE I
 ^1H Chemical Shifts of the Reagents and Products

Structure			$\delta(\text{ppm})$			
a'	b'	c'	a'	b'	c'	
			0.935	1.585	3.59	
			0.885	1.64	4.26	
			<i>i</i> 10, <i>i</i> 20 6.15, 5.59	<i>j</i> 0 1.95	<i>k</i> 20 4.25	<i>k</i> 10 3.84
			<i>i</i> 1', <i>i</i> 2' 6.13, 5.59	<i>j</i> ' 1.95	<i>k</i> ' 4.40	
			<i>i</i> 1, <i>i</i> 2 6.15, 5.59	<i>j</i> 1.95	<i>k</i> 2 4.30	<i>k</i> 1 4.30
					<i>k</i> 4.40	

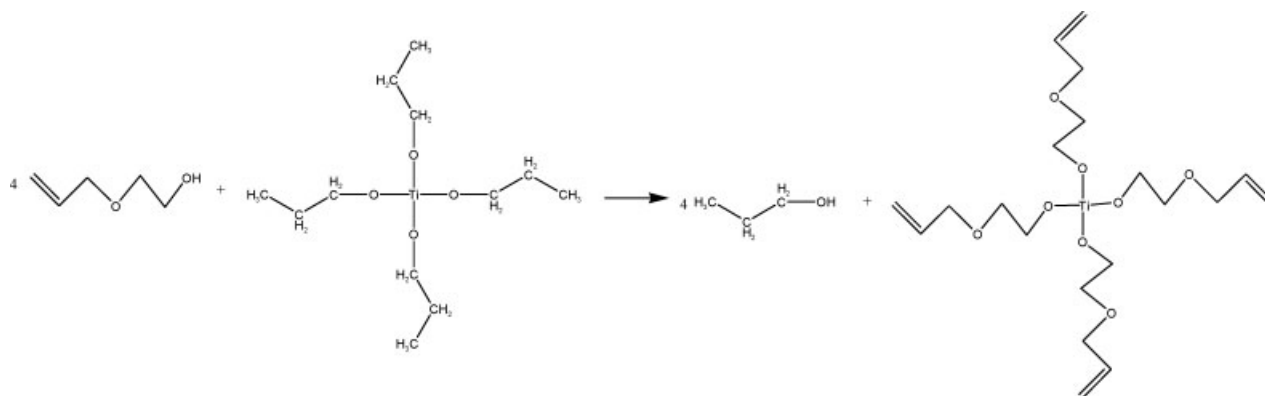
results suggested that the radical polymerization of methacrylate was not performed during the reaction.

In the range 3.8–4.5 ppm (part C), there were different peaks corresponding to the response of H's other than from CH₃ and the unsaturated group. They were composed of the CH₂ of the glycol group connected by two Ti atoms, the CH₂ of HEMA (unreacted HEMA and the HEMA group contained on the modified initiator), and the CH₂ of EGDMA. The integration of protons in the three parts should have been part A/part B/part C = 3 : 2 : 4 if the ester-ester exchange reactions were absent, even with an excess of free HEMA. However, the ratio (part A/part B/part C = 3 : 2 : 4.96) increased [Fig. 4(b)]. The value of part C increased with a longer reaction time. This allowed us to conclude that transesterification reactions were performed. Indeed, EGDMA had two segments of CH₂=CH(CH₃)CO— and only one segment of —O—CH₂—CH₂—O—, so

the ratio of the three parts changed in the synthesized initiator because the side product (EGDMA) was eliminated by distillation.

The ^1H -NMR result of the products was confirmed by TGA by the determination of the TiO₂/initiator ratio, which depended on the applied reaction time during the synthesis of the initiator. The principle of this method was to determine the titanium content after the degradation of the organic part of the initiator in the presence of water. The thermal degradation led to the formation of TiO₂.

At first, Ti(OPr)₄ was used. The molecular weight of Ti(OPr)₄ was 284 g/mol, the molecular weight of TiO₂ was 80 g/mol, and the theoretical ratio of TiO₂/Ti(OPr)₄ was 28.17%. The TGA result was 27.98%, which was very close to the theoretical value. The ratio 27.98 : 28.17 = 99.3% gave the purity of the commercial reagent (>98%). Then, modified initiator was used. The molecular weight of the



Scheme 4

theoretical $\text{Ti}(\text{OHEMA})_4$ was 564 g/mol, and the ratio $\text{TiO}_2/\text{Ti}(\text{OHEMA})_4$ was 14.18%. Two TGA results were 15.8 and 22.1% (for different reaction times during the synthesis of the initiator: 1 and 2 h, respectively). These values were different from the theoretical value (14.18%), and this could be explained by the ester-ester exchange reactions (Scheme 3). In this case, the functionality of the initiator was equal to $\text{Ti}(\text{OHEMA})_{4-x}$ (where x is a number that increased with the reaction time and represented the $\text{Ti}-\text{OCH}_2\text{CH}_2\text{O}-\text{Ti}$ bonds). In this case, the ratio $\text{TiO}_2/\text{Ti}[(\text{OHEMA})_{4-x}(\text{OCH}_2\text{CH}_2)_x]$ was superior to the theoretical ratio $\text{TiO}_2/\text{Ti}(\text{OHEMA})_4$.

The reactions with HEMA were out of control. So, we tried to use an alcohol reagent without an ester group to carry out the modification.

Modification by AEOH

The modification reaction is shown in Scheme 4.

The analysis by GC-MS of the condensed material extracted (Fig. 5) showed only the presence of propanol and the excess of AEOH. The GC-MS result proved that the modification was carried out accord-

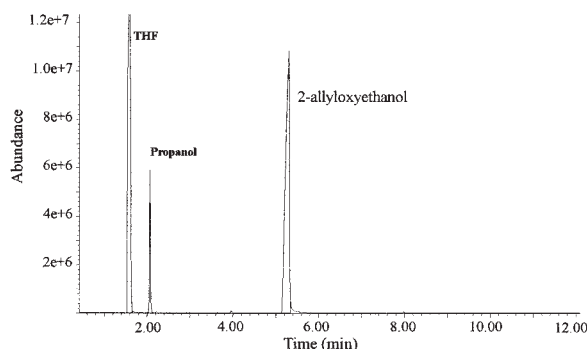


Figure 5 GC-MS spectra of the volatile fraction of the reaction of $\text{Ti}(\text{OPr})_4$ with AEOH.

ing to Scheme 4. The NMR results of $\text{Ti}(\text{AEO})_4$ and AEOH are shown in Figure 6. Their chemical shifts are shown in Table II. Figure 6(a) indicates that there was a very small quantity of unreacted $\text{Ti}(\text{OPr})_4$ in the final product, but the content was less than 1% (2.8/3/100, the peak at 0.90 ppm was the response of the CH_3 group of propoxide, and the peak at 5.9 ppm was the response of one proton of the double bond of the modified initiator). However, the integration of peaks E1 : E2 : E3 : E4 : E5 was equal to 2 : 1 : 2 : 2 : 2, which confirmed the chemical structure of our initiator. The allyl group was stable during the reaction, and no side reaction was found. The product was a $\text{Ti}(\text{AEO})_4$ with four unsaturated functionalities.

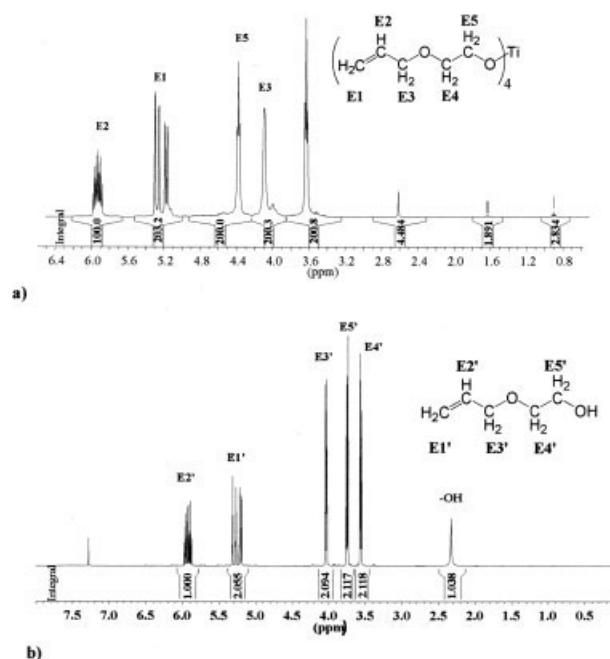
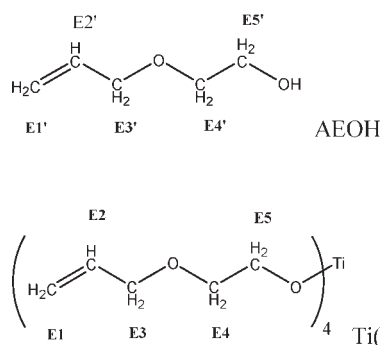


Figure 6 ^1H -NMR spectra of the (a) $\text{Ti}(\text{AEO})_4$ product and (b) AEOH reagent.

TABLE II
¹H Assignments and Chemical Shifts of Different Hydrogens in AEOH and Ti(AEO)₄



AEOH	E1'	E2'	E3'	E4'	E5'
δ ¹ H	5.19–5.31	5.89–5.96	4.04	3.56	3.75
Ti(AEO) ₄	E1	E2	E3	E4	E5
δ ¹ H	5.19–5.31	5.89–5.96	4.11	3.64	4.40

Study of the polymerization

The ROP of CL initiated by alkoxides and organometallic derivatives of transition metals of groups III and IV, such as zinc, tin, germanium, aluminum, and titanium, proceeds through a coordination–insertion mechanism.²⁷

The polymerization of CL was performed in a reactor to confirm the character of the pseudoliving polymerization catalyzed by Ti(AEO)₄. In the homopolymerization of CL, the molar mass of the polymer increased with the rate of conversion, but the molar mass distribution had a propensity to be broader at substantially higher monomer conversions (Table III).

The molar mass of the polymer increased as a function of conversion, as presented in Figure 7.

The necessity to divide the equation by four to have comparable values with experimental ones indicated the presence of four active sites on the initiator:

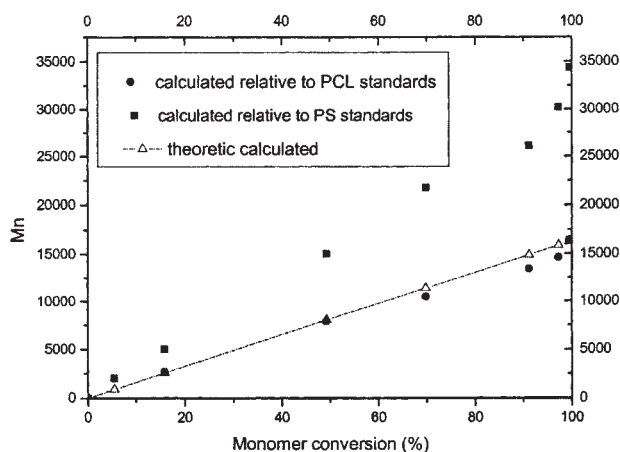


Figure 7 M_n versus monomer conversion.

$$M_n^{\text{theo}} = [(\% \text{ conversion}/100) \times ([M]_0/[I]_0) \times 114]/4$$

where M_n^{theo} is the theoretical number-average molecular weight, $[M]_0$ is the initial monomer concentration, and $[I]_0$ is the initial initiator concentration.

After the verification of the pseudocontrolled polymerization of CL with the new initiator, NMR was applied to verify that the double bonds at the end of the PCL arms did not react during the polymerization. The NMR results of one sample, shown in Figure 8, show that the ratio of CH of the double bond to the CH₂ of the CL unit was approximately equal to 1:2. With the use of the number-average degree of polymerization (DP_n) determined by SEC ($DP_n = 93$), the ratio was equal to $0.44:(95:93) = 0.44$. This result showed the presence of the double bond, which globally indicated that unsaturated group had not been opened by a thermal radical polymerization.

Polymerization in the twin-screw extruder

The SEC results (Table IV) show that the molecular weight of each single arm of the products from the

TABLE III
CL Conversions at Different Polymerization Times and the Molecular Weights Determined by SEC

Polymerization time (min)	Conversion of CL (%)	Calibrated by PS standards			Calibrated by PCL standards			$M_n^{\text{PCL}}/M_n^{\text{PS}}$
		M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	
1	6	2,000	2,400	1.2	—	—	—	—
1.5	16	5,000	6,000	1.2	2,700	3,200	1.2	0.5
2	49	15,000	30,600	2.0	7,900	13,800	1.7	0.5
2.5	70	21,800	46,400	2.1	10,500	20,000	1.9	0.5
3	91	26,000	61,000	2.3	13,000	26,000	2	0.5
5	97	30,000	66,000	2.2	14,600	27,900	1.9	0.5
12	99	34,000	74,000	2.2	16,400	30,800	1.9	0.5

CL/initiator = 572 (molar ratio); theoretical $DP_n = 143$; temperature = 125°C.

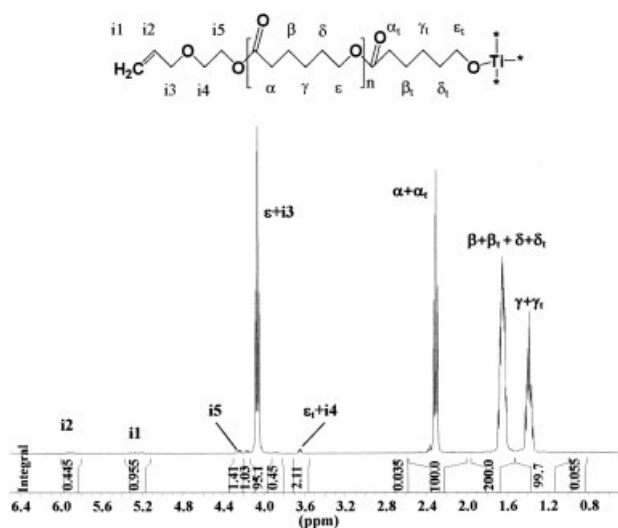


Figure 8 ¹H-NMR spectrum of the synthesized PCL (DP_n = 93, reaction time = 18 min, temperature = 125°C).

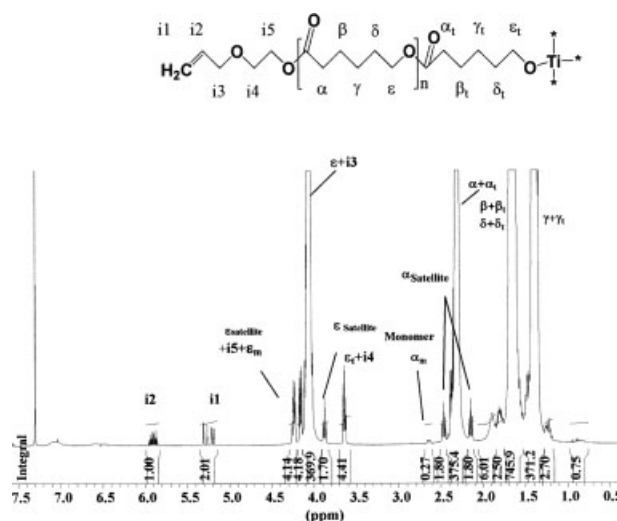


Figure 9 ¹H-NMR spectrum of the J3 extrudate sample (reaction time = 3 min, temperature = 180°C).

extruder was very near to the theoretical value, which indicated that there were four active sites on the initiator because the molecular weight was controlled by the feed concentration ratio of CL to the initiator. However, the polymerization of CL at high temperature and high conversion showed a higher polydispersity index generated by unsuitable side reactions (transesterification).

We had lots of exchange reactions with the initiator, and in these conditions, we had a pseudoliving polymerization but a good agreement between the observed molecular weights and those calculated with quantitative initiation assumed.

The ¹H-NMR results of sample J3 (Fig. 9) show that there was a little residual CL monomer, which was also proven by the SEC results. The quantity of the extrudate (by NMR spectroscopy) was $A_{\alpha m}/A_{\alpha} = 0.27/375.4 = 0.1\%$, so the conversion of CL in the extruder under the processing condition was very high, and the ROP reaction was completely achieved. Peaks *i1* and *i2* indicated that the double bond still existed after reactive extrusion.

Indeed, the NMR spectra showed that several peaks were present around 5–6 ppm, which indicated the presence of the allyl group. If the double bond were opened, a new assignment would be observed for H (*i1*) and H (*i2*), but H (*i5*) would

have stayed at its original position. The ratio of $A_{i1}/A_{i2}/A_{i5} = 2.01 : 1 : (4.14 - 1.70 - 0.27) = 2 : 1 : 2.17$ was near the theoretical ratio of 2 : 1 : 2, which indicated that most of the allyl function remained unchanged during the reactive extrusion. Therefore, DP_{n(NMR)} and the NMR-determined number-average molecular weight [$M_{n(NMR)}$] could be calculated as follows:

$$DP_{n(NMR)} = (\alpha + \alpha_t)/i1 = 375.4/2.013 = 184$$

$$M_{n(NMR)} = 114DP_{n(NMR)} = 114 \times 184 = 21 \times 10^3 \text{ g/mol}$$

where α and α_t correspond respectively, to the integral of CH₂ monomer unit and CH₂ of polymer unit. According to a comparison of this number-average molecular weight (M_n) value and the theoretical $M_{n(\text{feed})}$ value of 19.3×10^3 g/mol, these molecular weights showed the same trend.

CONCLUSIONS

We have described a method for the synthesis of functional PCL with a new initiator. Titanium alkoxide initiator with unsaturated function was prepared with unsaturated alcohol and titanium propoxide

TABLE IV
SEC Calculated Results for the Extrudates (with Calibration on PCL Standards)

Name	[CL]/[Ti(OAE) ₄] molar ratio	$M_{n(\text{feed})}$ (g/mol)	$M_{n(\text{SEC})}$ (g/mol)	$M_{w(\text{SEC})}$ (g/mol)	Polydispersity
J1	228	6,500	6,700	16,500	2.5
J2	448	12,700	13,200	25,600	1.9
J3	680	19,300	20,000	35,000	1.7

reagents. Functional polycaprolactone (PCL) was successfully synthesized and characterized by SEC and $^1\text{H-NMR}$. Depending on the initial monomer/initiator ratio, different polymers were obtained in a glass reactor and by a reactive extrusion process. Moreover, the polymerization was a quasiling process, and the M_n value of each polymer was close to that expected on the basis of the initial concentrations of the monomer and initiator and the conversion. However, the polydispersities were high and increased with the conversion, probably as a consequence of some transesterification reactions. The active end chain of polymers can be used to obtain tailor-made graft copolymers through the reaction between the end groups and unsaturated monomers, such as butyl acrylate, in a thermoplastic matrix.

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