In Situ Synthesis of Multiblock Copolymers of Poly(ε-caprolactone) with Different Poly(ether diols) Based Polyurethane by Reactive Extrusion

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ABSTRACT: Polyurethanes with multiblock copolymers of poly(ε-caprolactone) (PCL) and poly(tetramethylene oxide) glycol (PTMG) or poly(ethylene glycol) (PEG) as a soft segment were synthesized *in situ* via reactive extrusion from ε-caprolactone (CL) and 4,4′-diphenylmethane diisocyanate (MDI). The titanium alkoxide mixture generated from an ester-exchange reaction between titanium propoxide [Ti(OPr)$_4$], and excessive PTMG or PEG was used as an initiator and catalyst. Compared to the reported fabrication of polycaprolactone-based polyurethane (PCLU), the *in situ* reactive extrusion preparation not only explored a new rapid route for the fabrication of PCLU but also offered a simplified, controllable approach for the production of PCLU in a successive mass scale. A series of PTMG–PCLUs and PEG–PCLUs with different PCL block-average degrees of polymerization (DP$_n$'s) were prepared by only an adjustment of the relative concentration of CL in the reaction system, with a certain constant molar ratio of MDI to titanium alkoxide. ^{1}H-NMR, gel permeation chromatography, and differential scanning calorimetry results indicate that all of the CL monomers were converted in the polymerization, and the molecular weight of the copolymers was about 8×10^4 g/mol with a polydispersity index of approximate 2.4. With an increase in the PCL block-average DP$_n$ in PTMG–PCLU from 25 to 40, the tensile strength increased from 16.5 to 22.7 MPa, and the melting point increased from 46.1 to 49.5°C. It was also verified by PEG–PCLU prepared with organic Ti of lowered content in the initiator mixture that the mechanical properties could be greatly affected and dropped with decreasing content of organic Ti in the initiator mixture. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3765–3773, 2012

Key words: block copolymers; polyurethanes; reactive extrusion; ring-opening polymerization

INTRODUCTION

Poly(ε-caprolactone) (PCL) and its copolymers have attracted great interest as biodegradable materials bearing compatibility with cells over the past 2 decades.[1–4] The introduction of PU blocks into PCL chains as hard segments to form polycaprolactone-based polyurethane (PCLU) can improve the mechanical properties of PCL and expand its application in many fields, such as tissue engineering scaffolds, drug-delivery vehicles, and degradable sutures.[5,6] In general, the preparation of PCLU involves two steps, where PCL and PU are formed in separate steps. Typically, a PCL diol with a relatively low molecular weight is synthesized with an organic metal compound and a low-molecular-weight diol as an initiator and catalyst in the first step. In the second step, the PCL diol is rendered to react with diisocyanate followed by chain extension to form a PCLU of high molecular weight.[7–9] It was reported that it was feasible to fabricate PU via reactive extrusion, but a further chain extension was followed.[10–12] PCL can also be obtained by a one-step reactive extrusion.[13] Thus, it is possible to simultaneously perform the ring-opening polymerization of ε-caprolactone (CL) and the urethane reaction to form PCLU via one step in an *in situ* reactive extrusion with the proper initiator. This is anticipated to be a convenient, effective approach for synthesizing PCLU with the aid of the advantages of reactive extrusion technology.[14] In this study, we explored a novel method for realizing the copolymerization of CL and 4,4′-diphenylmethane diisocyanate (MDI), in which titanium alkoxide modified by poly(tetramethylene oxide) glycol (PTMG) or poly(ethylene
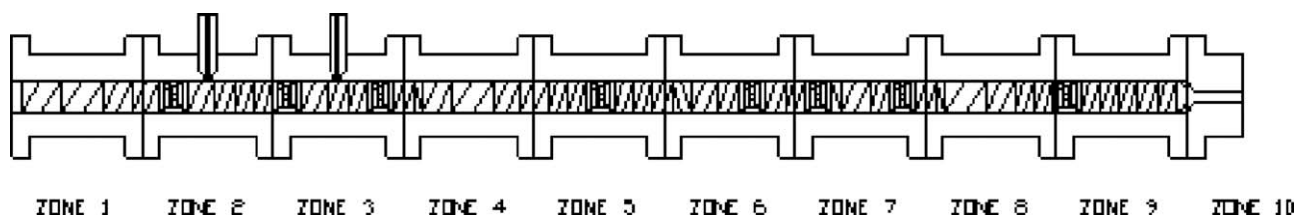
Figure 1 Schematic drawing of the screw for reactive extrusion.

glycol) (PEG) was used as an initiator and catalyst to successfully make PCLU multiblock copolymers containing PTMG or PEG (Guangzhou, China) in a corotating twin-screw extruder (Shanghai, China).

EXPERIMENTAL

Materials

CL (Solvey, Jiangsu, China), PEG [weight-average molecular weight (M_w) = 400 g/mol, functionality = 2], and PTMG (M_w = 1000 g/mol, functionality = 2) were purified by vacuum distillation at 100°C to remove absorbed water. MDI (Wanhua Corp.) and titanium propoxide [Ti(OPr)$_4$; Aldrich] were used as received.

Equipment

In the corotating twin-screw extruder with a movable barrel of 10 zones[15] (Shuangao Corp.), it was easy to clean, rearrange the screw blocks, and study the distribution of the product and reactants. The extruder was equipped with a set of weight monitor systems for reactants. The diameter of the screw was 35.6 mm, and the length-to-diameter ratio was 38 : 1, as shown in Figure 1. Liquid reactants could be fed into the barrel by a pump at any zone.

Piston metering pumps (Zhejiang Petrification Equipment Co., Ltd., Zhejiang, China flow rates = 0–6000 and 0–1500 mL/h, respectively) were used to pump the liquid reactants into the extruder.

Modification of Ti(OPr)$_4$

Ti(OPr)$_4$ (124.13 g, 0.5 mol) and excessive PTMG (4000 g, 4.0 mol) were charged into a three-necked flask equipped with a vacuum system and a mechanical stirrer. The reactants were allowed to undergo an ester-exchange reaction at 80°C for about 2 h. The produced low-boiling-point isopropyl alcohol was removed by a vacuum until there was no droplet distilled in the condenser. The produced the mixture of tetra-(poly(tetramethylene oxide) glycol) titanate Ti(OPTMG)$_4$ and remnant PTMG was cooled and sealed to preserve for further use. The modification of Ti(OPr)$_4$ by excessive PEG [molar ratio of Ti(OPr)$_4$ to PEG = 1 : 8] was carried out by the same procedure to get the mixture of tetra-poly (ethylene glycol) titanate Ti(OPEG)$_4$ and remnant PEG.

Reactive extrusion preparation of PCLU

PTMG–PCLU were synthesized via reactive extrusion in the corotating twin-screw extruder, in which the barrel temperature profile between the hopper and the die was190°C and the rotating speed was 100 rpm. A typical experimental procedure was as follows: calculated amounts of the PTMG-modified initiator mixture and MDI were dissolved in the CL monomer to make solutions A and B, respectively. Solutions A and B were pumped individually into the barrel at zones 2 and 3 by two pumps. The flow rates were controlled and monitored to ensure that the stoichiometric ratio of hydroxyl groups to isocyanate groups was 1 : 1, and the total flow rate of solutions A and B was 5 kg/h. The PTMG–PCLU products were extruded out of the die, cooled with cold water, dried by blasting, and cut into pellets. Products with different PCL block-average degrees of polymerization (DP_n's) were obtained by adjustment of the concentration of initiator in solution A and the control of the feeding ratio of solution A to solution B. PEG–PCLU could be prepared with the same procedure when Ti(OPTMG)$_4$ was substituted by Ti(OPEG)$_4$.

Measurements

#### Gel permeation chromatography (GPC)

The molecular weights and its distributions of the copolymers were analyzed with dimethylformamide as an eluent (flow rate = 1 mL/min at 30°C) with a GPC instrument (Waters 515, Massachusetts, US), equipped with a light-scattering instrument (Dawn Hellos, Wyatt Corp.), and a refractive index meter (Optilab, rEX), which were calibrated by polystyrene standards.

^{1}H-NMR

The ^{1}H-NMR spectra of the initiator and products were recorded on a Bruker Advance Digital 500-MHz instrument with deuterated chloroform (Aldrich): Shanghai, China (CDCl$_3$) as a solvent at 20°C.

Differential scanning calorimetry (DSC)

DSC was carried out over a temperature range from −100 to 200°C with TA DSC (Delaware, US) Q10
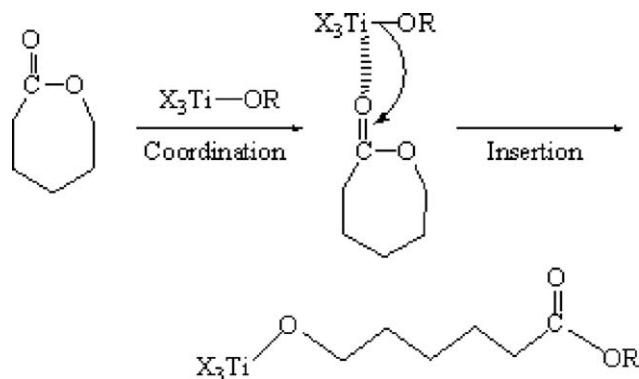
Scheme 1 Illustration of the coordination–insertion process of CL.

differential scanning calorimeter purged with nitrogen (50 mL/min). All samples were first heated to 100°C at 20°C/min, kept at 100°C for 3 min, cooled to −100°C at 10°C/min, and finally heated to 100°C at 10°C/min.

Tensile properties

The mechanical properties and elasticity of the products were determined with a new SANS CMT6104 electron (Shenzhen, China) tester at a draw rate of 100 mm/min at 20°C according to GB/T 528-1998.

RESULTS AND DISCUSSION

Synthesis mechanism of PCLU

The ring-opening polymerization (ROP) of CL can be initiated by titanium alkoxide, which involves CL monomer complexation to titanium alkoxide and insertion into the Ti—O bond (Scheme 1).[16–20] The ring opening of CL leads to the formation of a polyester chain capped with an active titanium alkoxide group at one end and an ester group carrying the alkoxy radical of the titanium alkoxide at the other end. The PCL chain propagates with the repeat of a coordination–insertion ring opening of CL monomers. Hydrolysis of the active titanium alkoxide bond can result in the formation of a hydroxyl end group. Therefore, the alkoxy segment of the initiator will characteristically remain at the end of the ultimate product, PCL; this technique was used by Xia et al.[13] to obtain PCL with unsaturated double bonds as end groups in an extruder. The end double bonds were introduced with a modified titanium alkoxide bearing double bonds.

In this work, Ti(OPr)$_4$ was modified via an ester-exchange reaction with excessive PTMG or PEG diol to be substituted for isopropyl alcohol, as shown in Eq. (1). (For convenience and simplicity, PTMG is used as an example in the following section.). The obtained titanium alkoxide, containing hydroxyl end

groups, was used as the initiator of the in situ polymerization of CL and the excessive PTMG diols. The four hydroxyl groups attached to each outer arm of the titanate remain at the end of the ultimate PCL obtained in this way [Eq. (2)]. However, every hydroxyl group might participate in the coordination via ester exchange with the metal atom of the alkoxy metallic compound to form a new alkoxy one [Eq. (3)]. This ester exchange suggests that the alkoxy group bonded with Ti atoms by σ bonds is a potential hydroxyl group to some extent, for the alkoxy group bonded with Ti is easily converted into a hydroxyl group when it encounters the active H atom of the free hydroxyl group:

$$\text{(1)}$$

$$\text{(2)}$$
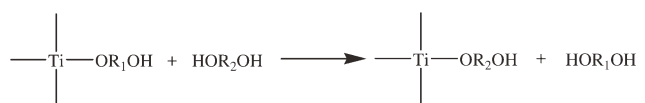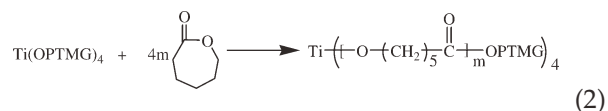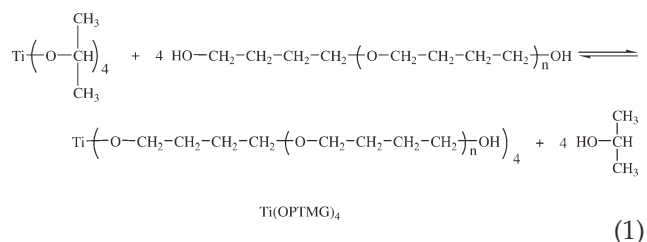
R$_1$ and R$_2$ are PTMG or PTMG-PCL copolymer chains with different $\overline{DPn}$.

$$\text{(3)}$$

$$\text{(4)}$$
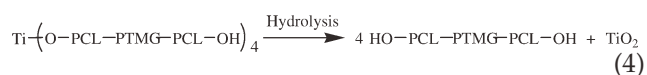
Therefore, all hydroxyl groups, including the potential hydroxyl group in the titanium alkoxide and the excessive free PTMG diols, which can still exchange with the alkoxy groups in titanate, will initiate the coordination–insertion ROP of CL via the Ti—O bond.[17–20] Namely, all hydroxyl groups can form chain carriers to initiate CL. Furthermore, the ester exchange ensures that every hydroxyl group of PTMG has an equal chance to propagate CL and that the formed PCL diol is linear with two free hydroxyl groups at the ends. The trace water in the system and the water for cooling the product will hydrolyze part of the PCL bonded with Ti as four arms to form a linear PCL diol with two free hydroxyl groups as ends [Eq. (4)]. Also, the remaining titanium alkoxide will act as the catalyst of the urethane reaction. Thus, the rest is the common urethane reaction between the PTMG–PCL copolymer diol and diisocyanate, and the formed PCLU is linear when the molar ratio of hydroxyl groups to isocyanate is kept at 1 : 1.
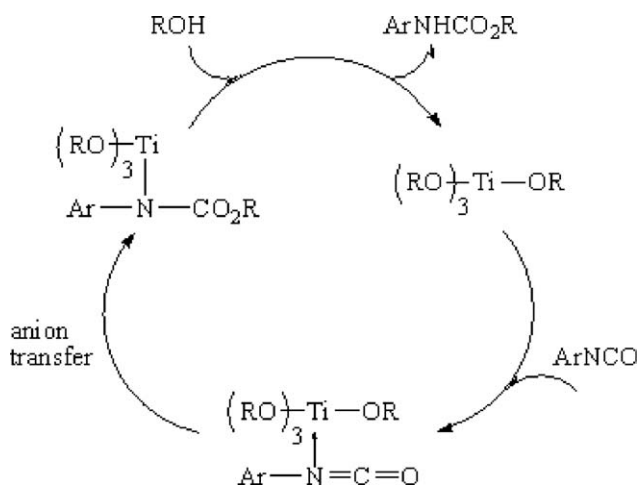
Scheme 2 Catalytic cycle of the formation of polyurethane (Ar = aromatic group).

The reaction of isocyanate and hydroxyl group should be catalyzed and accelerated by proper metallic compounds, such as bismuth octoate[21] or titanate[22] (alkoxy titanium), to meet the requirement of an extremely short residence time for reactions proceeding in an extruder to obtain a high-molecular-weight polyurethane.

The catalytic mechanism of the reaction of polyols and isocyanate groups catalyzed by metallic compounds can be described as a catalytic cycle (Scheme 2)[23] involving the N coordination of isocyanate with the alcoholysized titanium alkoxide and the transfer of the alkoxide anion onto the coordinated isocyanate to afford an N-titantyl urethane. The alcoholysis

of the N-titantyl urethane gives a urethane and the original alcoholysized titanium alkoxide. The repeat of the cycle results in polyurethane long chains. The titanium alkoxide acts as the catalyst of the urethane reaction.

Structure of the modified titanium alkoxide and PTMG–PCLU

^{1}H-NMR analysis of titanium alkoxide mixture

There were two peaks in the ^{1}H-NMR spectrum of $Ti(OPr)_4$, at 1.24 and 4.49 ppm, assigned to the protons of the methyl group (CH_3) and CH, respectively. The corresponding integral intensity ratio was about 6 : 1, which was consistent with the corresponding proton number ratio in the chemical structure (see Fig. 2). The spectrum of the mixture of $Ti(OPTMG)_4$ and PTMG was somewhat similar to that of PTMG (Fig. 3). The difference appeared at 3.62–3.65 ppm for e-protons because a quarter of the hydroxyl groups were bonded with Ti atoms. In the $Ti(OPTMG)_4$, the peaks for e-protons shifted to a slightly higher energy region. Because the isopropyl groups of $Ti(OPr)_4$ were exchanged [see Eq. (1)] and removed by the vacuum, the peaks at 1.24 ppm for the protons of CH_3 were depressed in the spectrum. The ratio of protons of CH_3 in the isopropyl groups (at 1.24 ppm) to the b,b'-protons in PTMG (at 3.41 ppm) decreased from the theoretical 1 : 16.85 to 0.0059 : 12.96; this meant that 99.2% of the isopropyl groups were exchanged by PTMG and removed. Thus, the product was a mixture of the obtained $Ti(OPTMG)_4$ and the remnant PTMG.
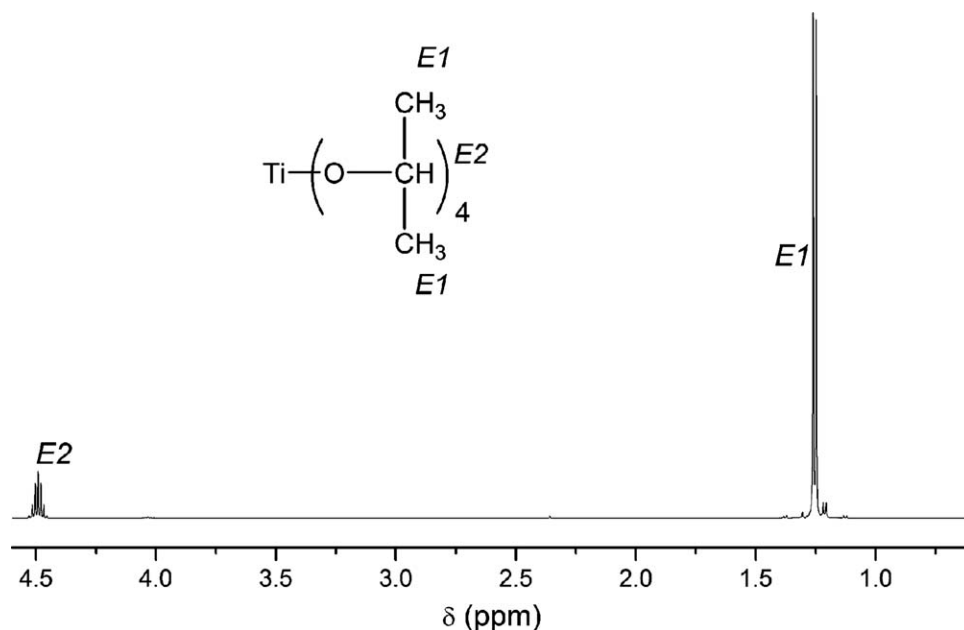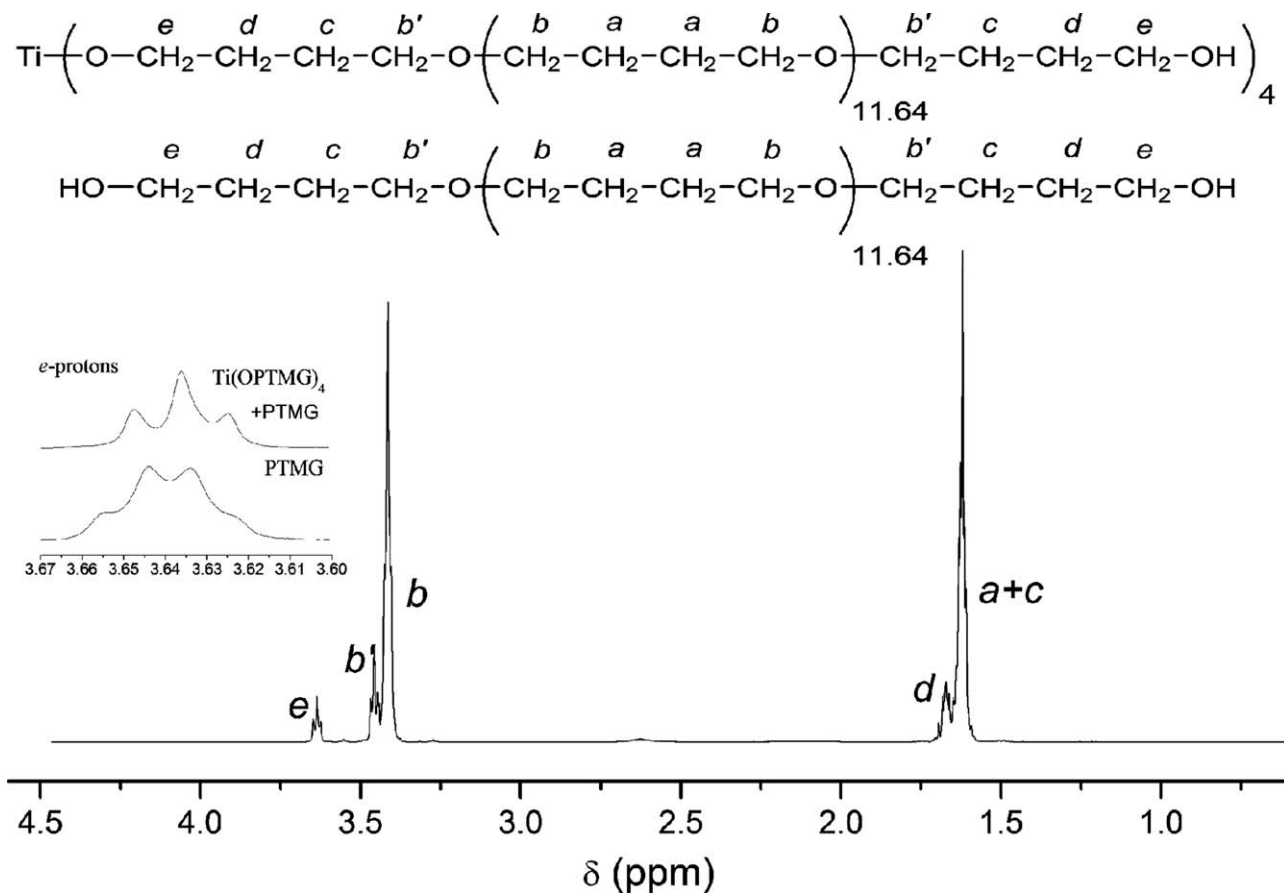

Figure 2 ^{1}H-NMR spectrum of $Ti(OPr)_4$ in $CDCl_3$.

Figure 3 ^{1}H-NMR spectrum of the mixture of PTMG and Ti(OPTMG)$_4$.

^{1}H-NMR of PTMG–PCLU

Figure 4 shows the chemical shifts of the protons of sample PTMG–PCLU with a PCL block (DP_n) of 25. The chemical shifts could be assigned to the protons of the blocks of copolymer.[18] The peak at 3.41 ppm corresponded to the *b*-protons of the two methylenes, which were adjacent to the oxygen atom in the repeat unit PTMG. Because the hydroxyl groups of PTMG were coordinated with Ti atoms and initiated the ROP of CL, the methylenes bonded with hydroxyl groups turned our to be bonded with the ester groups, which caused the chemical shift of *e*-protons to shift to a low-energy region as *e'*-protons. For instance, the chemical shift at 3.64 ppm for *e*-protons shown in Figure 3 disappeared in Figure 5 and shifted to about 4.15 ppm as *e'*-protons; this indicated that all of the PTMG participated in the copolymerization. Also, each PCL block had a *j*-methylene at one end bonded with MDI to form a urethane linkage; this caused the end *j*-protons to shift from 4.06 ppm to about 4.12 ppm to be *j'*-protons.

In the copolymer, the relative intensity integral ratio of *h*-protons of methylene in CL unit to the *e'*-protons of methylene in PTMG unit was 1.000 :

0.039 = 25.64; this was almost equal to the feeding ratio [CL]/[PTMG] × 2 = 25. The agreement indicated that the pump feeding was reliable and that the two ends of each PCL block in the PCLU were bonded with PTMG and MDI, respectively. The integral ratio of *m*-protons of MDI at 3.88 ppm to *e'*-protons of methylene in PTMG was 0.020 : 0.039 = 0.513. According to the reaction mechanism, the ratio of MDI to PTMG in the copolymer was 1.026; this was almost equal to the feeding ratio [MDI]/[PTMG] = 1 and ensured that the obtained copolymer was a linear, high-molecular-weight PTMG–PCLU.

From the results of GPC and ^{1}H-NMR analysis, we confirmed that the extruded products were multiblock copolymers with PTMG, PCL, and MDI as building blocks and that all of the feeding CL monomers were converted to PTMG–PCLU. Furthermore, almost all of the charged CL was polymerized at two ends of PTMG to form PTMG–PCLU with a relatively high molecular weight and narrow distribution, although there was only a trace mount of Ti(OPTMG)$_4$ in the initiator system. Thus, the PCL block DP_n in the copolymer could be calculated as [CL]/(2 × [PTMG]), according to the feeding ratio.
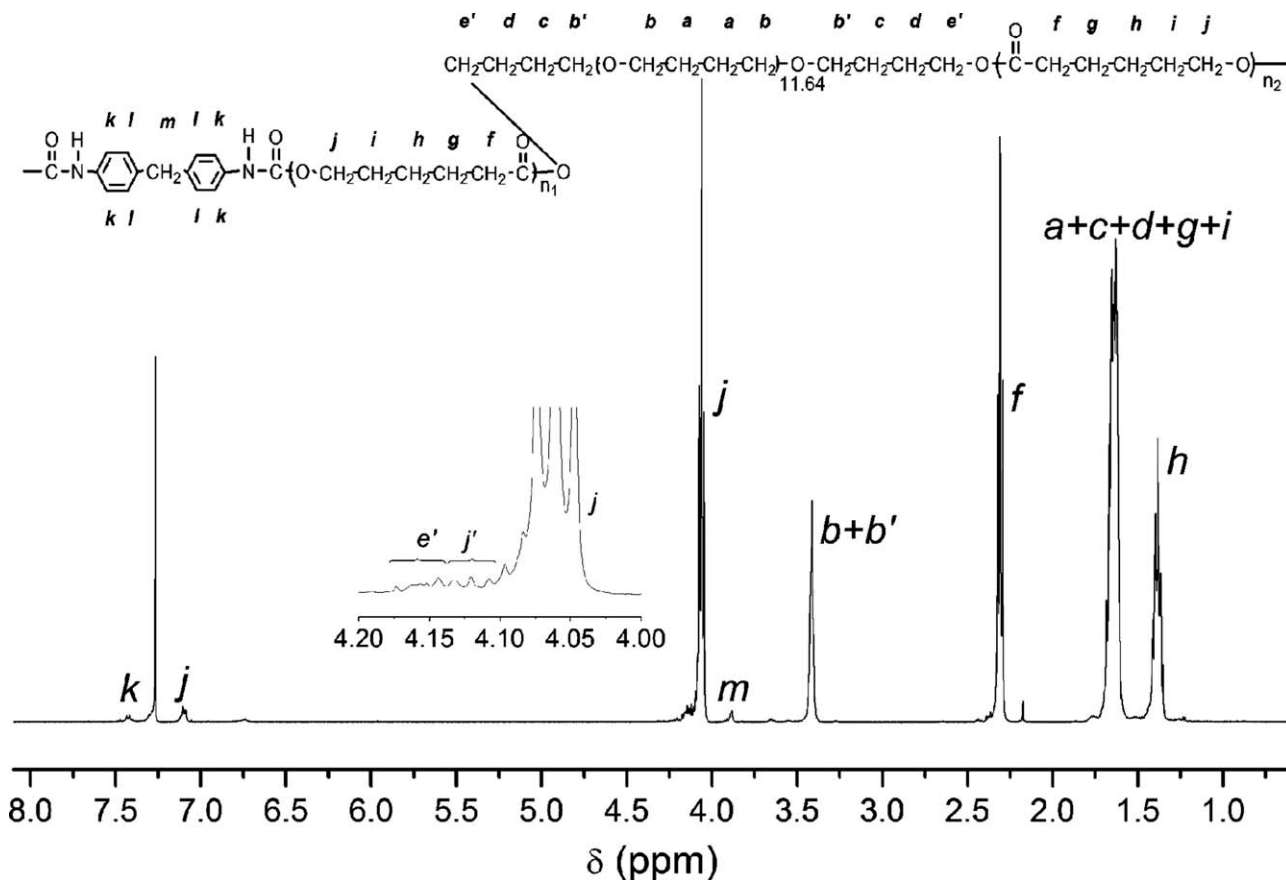
Figure 4 ^{1}H-NMR spectrum of PTMG–PCLU with a PCL block DP_n of 25.

Molecular weight and its distribution in PTMG–PCLU

The GPC results of PTMG–PCLU with different PCL block DP_n's, set by the feeding ratio of [CL] to [PTMG], are tabulated in Table I. With sample PCLU35 with a PCL block DP_n of 35 taken as an example, the nearly symmetrical unimodal distribution of the GPC trace indicated that the copolymerization was completed successfully and that there was no homopolymer in the product (Fig. 5). Furthermore, the molecular weight of the multiblock copolymer had a narrow distribution, with an approximate polydispersity index of 2.4. This was also confirmed by the ^{1}H-NMR results of the product (Fig. 4). There was almost no characteristic peak at 2.65 ppm for the protons of methylene bonded with the carbonyl group in the structure of the CL monomer; this indicated the depletion of the CL monomer. All of the charged CL was converted into copolymer. According to the polymerization mechanism, CL monomers were initiated to polymerize at two ends of PTMG to form a PCL–PTMG–PCL triblock copolymer with hydroxyl groups as two ends. Theoretically, the molecular weight (M) of a copoly-

mer obtained can be calculated as follows, on the basis of the feeding ratio:

$$M_{PCL} = M_{PTMG} + 2DP_n \times M_{CL}$$

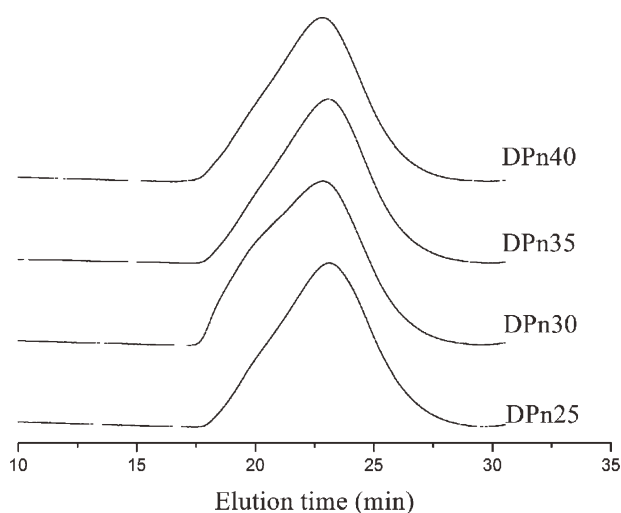**Figure 5** GPC profiles of the PTMG–PCLU products.

TABLE I
Composition and GPC Results of PTMG–PCLU

Sample	[CL]/2[PTMG] feed ratio (mol/mol)	[Ti]/[CL] (mol/mol)	DP_n of PCL block[a]	[MDI]/[PTMG] (mol/mol)[b]	M_n (10^3 g/mol)	M_w/M_n
PCLU25	25 : 1	1 : 400	25.64	1.03	75.5	2.42
PCLU30	30 : 1	1 : 480	30.63	1.04	82.6	2.58
PCLU35	35 : 1	1 : 560	35.38	1.02	84.8	2.35
PCLU40	40 : 1	1 : 640	39.54	0.98	88.6	2.42

[a] Average DP_n calculated according to the ^{1}H-NMR spectrum.
[b] Calculated according to the ^{1}H-NMR spectrum by the integral intensity ratio of the peak at 3.83 ppm for MDI to the peak at 4.15 ppm for PTMG.

where $1000_{(PTMG)} + 35 \times 114_{(CL)} \times 2 = 8.9 \times 10^3$ g/mol when there is no reaction between the end hydroxyl groups and diisocyanate to form urethane bonding. However, in our experiments, the number-average molecular weight (M_n) of the product measured by GPC was as high as 84.8×10^3 g/mol; this demonstrated that end hydroxyl groups reacted with diisocyanate. The strong mixing and dispersing capacity of the twin screw rendered all units to react with uniform probability to form products with a narrower molecular weight distribution. GPC traces of the rest products obtained by different feeding ratios (PCLU25, PCLU30, and PCLU40) were quite similar to that of PCLU35, as shown in Table I.

Properties of PTMG–PCLU and PEG–PCLU

Tensile properties

The tensile strength and elongation at break of the copolymer increased with increasing PCL block DP_n (as shown in Table II). Compared to the pure PCL, with a molecular weight of 6.0×10^4 g/mol (tensile strength = 50 MPa and elongation at break > 1000%), the tensile properties of PTMG–PCLU decreased when PTMG and the urethane linkage were introduced into the molecular chain. However, the tensile strength and elongation increased with increasing PCL content and decreasing PTMG content in the PCLU; this was similar to that of the product obtained with a two-step method by Heijkants et al.[9]

It was also found that tensile properties of PTMG–PCLU with a PCL block DP_n of 40 decreased slightly

compared to PTMG–PCLU with a PCL block DP_n of 35; this resulted, to some extent, from the relatively low organic Ti content as an initiator for the polymerization of CL. As discussed previously, a relatively low content of organic Ti can still initiate the polymerization of CL, and there is still no CL monomer in the extrusion product; this means that all charged CL was converted to PCL in PTMG–PCLU. However, the relatively low content of organic Ti affected the addition polymerization of hydroxyl and isocyanate groups and the high viscosity in the reaction system, of which the torque applied to the screw increased from 45 N m to about 60 N m.

To investigate the effect of the low content of organic Ti on the tensile strength of PCLU, PEG–PCLU in which PEG was substituted for PTMG in the copolymer was prepared by the same method. Figure 6 shows the tensile strength of PEG–PCLU plots with different PCL block DP_n's. It was a similar trend that the tensile strength of PCLU dropped after the PCL block DP_n increased to more than 35. Another series of PEG–PCLUs was prepared to verify this phenomenon where the PCL block DP_n was set at 30 but the organic Ti contents of the initiator mixture were varied as 1 : 8, 1 : 16, 1 : 32, and 1 : 64

TABLE II
Tensile Properties of PTMG–PCLU

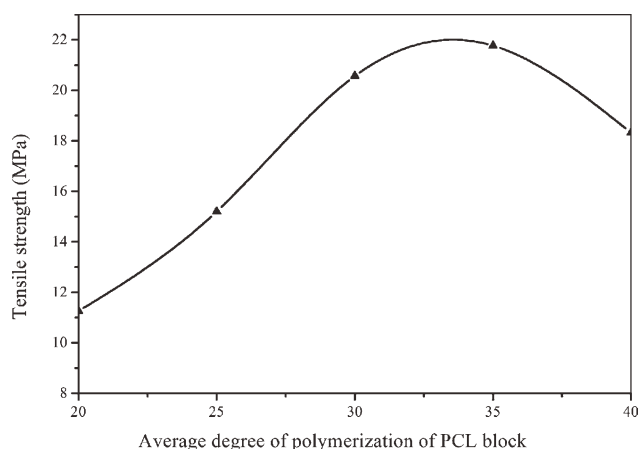| Sample	PCL block DP_n	Tensile strength (MPa)	Elongation at break (%)
PCLU DP_n 25	25	16.5	1030
PCLU DP_n 30	30	16.8	781
PCLU DP_n 35	35	22.7	1023
PCLU DP_n 40	40	21.7	787

Figure 6 Influence of different PCL block DP_n values on the tensile strength of PEG–PCLU.

(the molar ratio of Ti to PEG). As anticipated, the tensile strength of the PEG–PCLU of the same PCL block DP_n decreased with decreasing organic Ti content of the initiator mixture (Fig. 7). With decreasing organic Ti of the initiator mixture, the ratio of organic Ti to CL monomer dropped drastically, as shown in Figure 7. The ratio of organic Ti to CL monomer decreased much more than that of PEG–PCLU with PCL block DP_n's from 35 to 40. The reduced organic Ti effectively initiated the polymerization of CL, but the uniformity of the products was depressed because the organic Ti with a lowered content could not effectively catalyze the urethane reaction. This was also verified by the GPC results, in which the polydispersity index of the products increased, from 2.4 to 5.7, with a decrease in organic Ti. The occurrence of weak sites resulted from the lesser uniformity of the products and led to a decrease in the tensile strength. Therefore, the tensile strength of PTMG–PCLU and PEG–PCLU deceased with increasing PCL block DP_n to greater than 30–35 when the organic Ti content in the polymerization system was reduced to a certain level.

DSC analysis of PTMG–PCLU

The melting and crystallization behaviors of the PTMG–PCLU multiblock copolymers were investigated by DSC. Figure 8 shows the DSC curves. All of the samples had a glass-transition temperature around 63°C. They all had a monomodal endothermic peak in the second heating run with a crystalline melting temperature (T_m) within 46 to 49°C. In more detail, the glass-transition temperature of PTMG–PCLU decreased with increasing PCL block DP_n, whereas T_m and the melt enthalpy increased. This implied that the crystal of PCL tended to be more perfect with increasing PCL block DP_n. How-
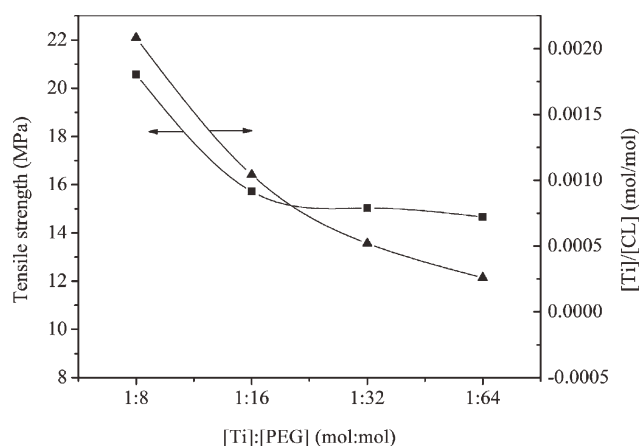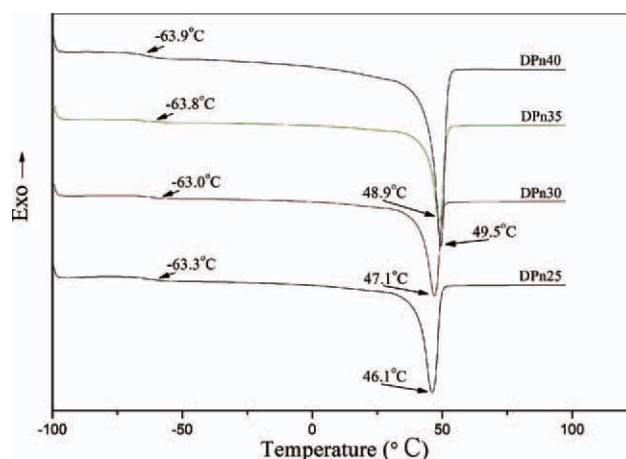

Figure 8 DSC curves of PTMG–PCLU with different PCL block DP_n values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ever, the T_m and melt enthalpy of PTMG–PCLU were lower than those of pure PCL (54.91°C and 72.21 J/g, respectively). The difference between the crystals of PCLU and pure PCL resulted from two aspects. First, compared to pure PCL, the lower molecular weight of the PCL block led to less perfect crystals of PCL in the copolymer. On the other hand, the PTMG segment blocked in the copolymer restricted the crystallization of the PCL chain, which also led to less perfect crystals in PCL. However, the effect of restriction decreased with increasing PCL block DP_n. It was favorable that T_m could be adjusted by the setting of DP_n of the PCL block and introduction of PTMG into the molecular chain. In turn, the crystallization of PTMG was also restricted by the block of PCL.[4,24,25] Thus, the melt peak of PTMG blocks disappeared in the discussed range of PCL block DP_n's, from 25 to 40.

CONCLUSIONS

PTMG–PCLU and PEG–PCLU with relatively narrow molecular weight distributions were prepared *in situ* via reactive extrusion initiated by a mixture of PTMG (or PEG) and Ti(OPTMG)$_4$ [or Ti(OPEG)$_4$]. By adjusting the molar ratio of CL to PTMG (or PEG), we obtained a series of PCLUs with different PCL block DP_n's. The tensile strength of the obtained PTMG–PCLU increased from 16.5 to 22.7 MPa, and T_m increased from 46.14 to 49.45°C with increasing PCL block DP_n in PTMG–PCLU from 25 to 40. The mechanical properties could be greatly affected by the content of organic Ti in the initiator mixture. It was confirmed by PEG–PCLU with a PCL block DP_n of 30 that the tensile strength of PCLU dropped with decreasing content of organic Ti in the initiator mixture.

Figure 7 Influence of organic Ti content of the initiator mixture on the tensile strength of PEG–PCLU with the PCL block DP_n of 30.

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