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ORIGINAL PAPER

Lipase Catalyzed Synthesis of Poly(ε-Caprolactone)−Poly(Dimethylsiloxane)−Poly(ε-Caprolactone) Triblock Copolymers

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Abstract Immobilized lipase B from *Candida antarctica* was used to synthesize copolymers of poly(ε-caprolactone) (PCL) with α,ω-(dihydroxy alkyl) terminated poly(dimethylsiloxane) (PDMS). The reactions were carried out in toluene with a 1:2 w/v ratio of the monomers to solvent at 70ºC. The PCL−PDMS−PCL triblock copolymer composition was varied by changing the feed ratio of the reactants [CL]/[PDMS] (80:20; 60:40; 40:60; 20:80 w/w, respectively). The enzymatically synthesized copolymers were characterized by GPC, FTIR, TGA, DSC and XRD. The successful synthesis of the copolymers was confirmed by the appearance of a single peak in all of the respective GPC chromatograms. An increased feed ratio of [CL]/[PDMS] produced an increase in the number-average molecular weight (M_n) of the copolymers from 4,400 $g mol^{-1}$ (20:80 w/w of [CL]/[PDMS]) to 13,950 $g mol^{-1}$ (80:20 w/w of [CL]/[PDMS]). The copolymers were shown by DSC and XRD to be semi-crystalline and the degree of crystallinity increased with an increase in the [CL]/[PDMS] feed ratio. The crystal structure in the copolymers was analogous to that of the PCL homopolymer. In enzymatic polymerization the recovery and reuse of the enzyme is highly desirable. When the lipase was recovered and reused for the copolymerization, higher molecular weight copolymers were obtained upon a second use. This appears to be due to an increased activity of the immobilized lipase following an opening up of the acrylic resin matrix in the organic medium. This improvement was not maintained for subsequent recycling of the lipase principally due to the disintegration of the acrylic resin matrix.

Keywords Lipase · Copolymers · Poly(ε-caprolactone) · Poly(dimethylsiloxane)

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1 Introduction

Research on enzymatic polymerizations is receiving increased attention in the 21st century due to the fact that "green" pathways to new materials are growing in importance. Enzymatic polymerization is an environmentally friendly approach to polymer synthesis and it may be contrasted with traditional chemical methods, which often require harsh conditions and metal containing catalysts. It is typically required that residual catalysts and solvents be completely removed for biomedical, pharmaceutical and personal care applications [1-4]. Biodegradable polymers have generated an enormous amount of research interest in the fields of biomedical, agricultural and industrial applications [5]. One such example is poly(ε-caprolactone) (PCL), which is a semi-crystalline homopolymer having a glass transition temperature of −60ºC and melting point in the range 59 to 64ºC, depending upon the crystalline nature and thermal history of the PCL. Due to its slow biodegradation, PCL is ideally suited for long-term drug delivery extending over a period of more than one year [6]. Silicon-containing block copolymers are particularly interesting because of the unique properties of polysiloxanes. The exceptional properties of poly(dimethylsiloxane) (PDMS), such as a very low glass transition temperature

(−120ºC), low surface energy, high gas permeability, resistance to oxidation, biocompatibility, etc. lead to materials for a wide range of potential applications [7, 8]. Furthermore, silicone polymers have been applied in a wide range of medical devices, such as blood oxygenators, contact lenses, finger joints, catheters, blood pumps, breast implants, tubing, ophthalmologic implants, adhesives, tissue expanders and heart valves [9].

Recently, poly(ε-caprolactone)-block-poly(dimethylsiloxane)-block-poly(ε-caprolactone) triblock copolymers (PCL-*b*-PDMS-*b*-PCL) were synthesized by Xu and Zheng *via* the ring-opening polymerization (ROP) of ε-caprolactone (CL) in the presence of 3-hydroxypropyl-terminated PDMS (HTPDMS). The resulting triblock copolymers were incorporated into epoxy thermosets in order to prepare nanostructured thermosetting blends [10]. In their system, stannous octanoate was used as the catalyst at 120ºC. Normand and coworkers have reported that 120ºC is the maximum use temperature for stannous octanoate in siloxane polymerizations. However, the above method has a major problem in that deactivation of the tin(II) catalyst occurs above 100ºC in the presence of oxygen (air) [11].

Several authors have reported the enzymatic copolymerization of PCL and PDMS with various other monomers/polymers such as poly(ethylene glycol), alkyl diacids/diols and sugars [5, 12-14]. However, to our knowledge the enzymatic copolymerization of PDMS with ε-caprolactone has not been reported in the literature. Copolymerization of CL with monohydroxyl or dihydroxyl poly(ethylene glycol) (PEG) has been performed using Novozyme-435 (immobilized lipase B from *Candida antarctica*) as a catalyst [7]. The resulting copolymers were shown to be semi-crystalline. Solution cast films were found to degrade in a pH 7.0 phosphate buffer solution containing *Pseudomonas lipase*. The weight loss data showed that the introduction of PEG segments into the PCL main chain did not significantly alter the enzymatic degradation of PCL.

Bishwabhusan et al. [12] have performed the lipase-catalyzed esterification of organo-siloxane carboxylic diacids and the C1-O-alkylated α,β-ethyl glucoside. The organo-siloxane-sugar conjugates were prepared in a one-step reaction without protection-deprotection steps and without the activation of the acid groups. A finding of major significance is the fact that the integrity of the siloxane bonds was maintained. Sharma et al. [13] have reported lipase-catalyzed synthesis of silicone polyesteramides in the bulk at 70°C under reduced pressure (10–20 mmHg). Immobilized *Candida antarctica* lipase B (Novozyme-435) was used as the enzyme under mild reaction conditions to perform the polycondensation reaction using various feed mole ratios of diethyl adipate, 1,8-octanediol, and α, ω-(diaminopropyl) poly(dimethylsiloxane).

Recently, we have reported the synthesis of silicone polyesters by the condensation polymerization of 1,3-bis(3-carboxypropyl)tetramethyldisiloxane with various alkanediols (1,4-butanediol, 1,6-hexanediol and 1,8-octanediol). These reactions were carried out in the bulk in the temperature range 50 – 90°C under reduced pressure (50–300 mmHg vacuum gauge) using lipase B from *Candida antarctica* as the catalyst. The effect of reaction temperature, vacuum, enzyme activity, and enzyme concentration on the reaction kinetics were investigated and the details have been reported elsewhere [14]. The physical properties of the siloxane polyesters are currently being investigated.

In the present study, we report (i) the enzymatic synthesis and (ii) the characterization of PCL−PDMS−PCL triblock copolymers. The copolymerization was performed using immobilized lipase B from *Candida antarctica* as the catalyst in toluene at 70ºC. The PCL−PDMS−PCL triblock copolymer composition was varied by changing the feed ratio of the reactants [CL]/[PDMS] (80:20; 60:40; 40:60; 20:80 w/w, respectively). The copolymers were characterized by Gel Permeation Chromatography (GPC), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and X-Ray Diffraction (XRD).

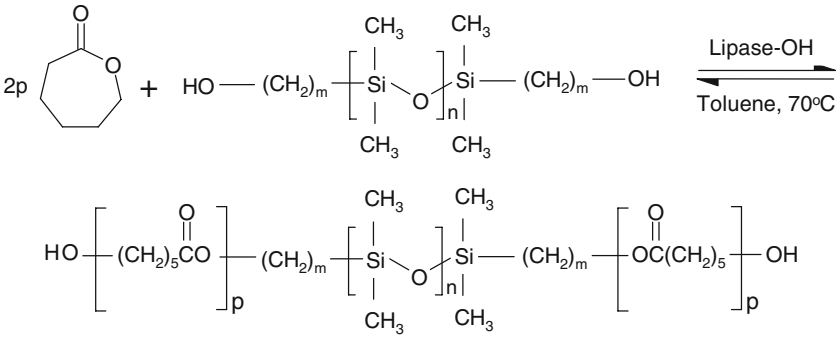
2 Experimental

2.1 Materials

All chemicals were analytical grade and were used as received. Immobilized lipase B from *Candida antarctica* (Lot#047K1672 with activity 11,200 PLU (propyl laurate units/g)) and ε-caprolactone (CL) were purchased from Aldrich Co. HPLC/Spectro grade toluene and tetrahydrofuran (THF) were purchased from Tedia Co. Inc. The α,ω-(dihydroxy alkyl) terminated poly(dimethylsiloxane) (PDMS) (TEGOMER® H-Si 2311, M_n=2500 gmol^{-1}, PDI (M_w/M_n)=2) was a gift from Degussa.

2.2 Synthetic Methods

Before starting the reaction shown in Scheme 1, the monomers at 70ºC and the enzyme at room temperature were dried under vacuum (400 mmHg vacuum gauge) for 24 h. Lipase B from *Candida antarctica* (10% by wt. of the monomer and/or polymer) was transferred into a round bottom flask (25 mL flask) containing the monomers (1 g of monomers with varied feed ratios of CL/PDMS: 100/0; 80/20; 60/40; 40/60; 20/80 by w/w, respectively). The reactions were performed in toluene a 1:2 v/w ratio of the monomers to solvent at 70ºC. The flask was capped with an adaptor and placed in an oil bath maintained at the desired



Scheme 1 Lipase catalyzed copolymerization of ε-caprolactone with α, ω-(dihydroxy alkyl) terminated PDMS (m≈7, n≈30 and M_n≈ 2500 gmol^{-1}) in toluene at 70 °C

temperature (± 0.1 ºC). The reaction contents were mixed with a magnetic stirrer. Aliquots of about 5 mg were removed from the reaction mixtures after 4½ h and dissolved in 1 mL of THF solvent in different glass vials. The enzyme was removed by filtration using a glass-fritted filter (medium porosity). Gel Permeation Chromatography (GPC) was used to characterize the product molecular weight (M_n) and molecular weight distribution (M_w/M_n).

The residual enzyme activity was determined by the esterification of 1-octanol and lauric acid in isooctane at 37ºC. The formation of the product octyl laurate was detected and quantified using Gas Chromatograph (GC).

2.3 Instrumental Methods

Molecular weights of the various copolymers were determined by GPC using a Shimadzu LC-20AT pump, a RID-10A refractive index detector, and a Phenogel GPC 300 x 7.8 mm×5 μm column. THF was used as an eluent at a flow rate of 1.0 ml/min. Sample concentrations of 5–10 mg/mL and injection volumes of 50–100 μl were used. Narrow polystyrene standards with molecular weights ranging from 550 to 480,000 gmol^{-1} (Millipore, Waters Chromatography Division, MA 01757) were used to calibrate the system. The system calibration data was acquired and relative molecular weight calculations were processed using Shimadzu Class-VP software.

Wide-angle X-ray Diffraction (WAXD) was performed using X′ Pert PRO, Cu K_α radiation, with a wave length of λ=0.154 nm. The experimental setup included a linear detector for acquiring 1D WAXS measurement distance of 32 cm. WAXD of PCL−PDMS−PCL triblock copolymers were obtained by setting a step size of 0.025 and time per step of 1 sec with a scattering angle 2θ ranging between 10 to 30º.

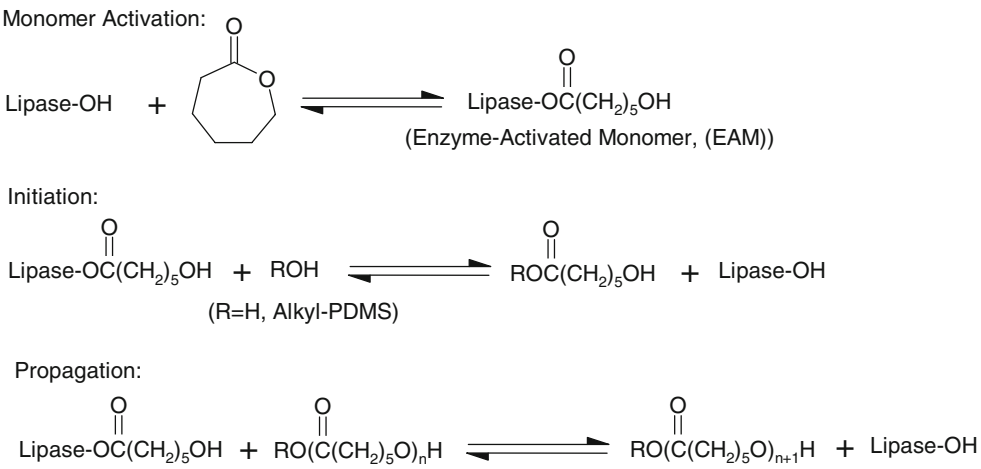
Thermogravimetric Analysis (TGA) was performed in a nitrogen atmosphere by means of a TA Instruments TGA2050 Thermogravimetric analyzer. The measurements were carried out with a heating rate of 10 °C/min and temperature ranging from room temperature to 800 °C. Differential Scanning Calorimetry (DSC) analysis was performed using a TA Instruments 2010 DSC. DSC scans were run in the temperature range from −150 to 150 °C at 10 °C/min. A controlled cooling rate of −10 °C/min was applied between heating runs.

The enzyme activity was determined by the esterification of 20 mg of 1-octanol and lauric acid (1:1 mole ratio) catalyzed by 10 mg of the recovered lipase in 1 ml of isooctane at 37ºC for 1 h. The amount of product octyl laurate formed was analyzed by Gas Chromatography (GC). About 1 μl of reaction sample was injected into the GC (Shimadzu GC-2010) 0.5 μm x 0.25 mm x 15 m SHRX5 capillary column, split injection at 200ºC, flow rate 30.4 ml min^{-1}, FID detector 350ºC, ramp of 75–300ºC over 18 min. The residual enzyme activity was determined from the relative peak areas of the product octyl laurate formed by the pure and the recovered lipase. The data was acquired and processed using Shimadzu Class-VP software.

3 Results and Discussion

Lipase-catalyzed reactions are proposed to proceed *via* an acyl-enzyme intermediate [15]. The enzymatic polymerization of lactones may be explained by considering the following reactions as the principal reaction course (see Scheme 2). The catalytic site of the lipase is known to be a serine-residue. The key step is the reaction of the lactone with lipase involving the ring-opening of the lactone to give the acyl-enzyme intermediate (Enzyme-Activated Monomer, EAM). The initiation is by nucleophilic attack of water, which is probably contained in the enzyme or in the reaction mixture, onto the acyl carbon of the intermediate to produce ω-hydroxycarboxylic acid (n=l), the shortest propagating species. In the propagation stage, the intermediate is nucleophilically attacked by the terminal hydroxyl group of a propagating polymer to produce a one-unit-more elongated polymer chain. The rate-determining step of the overall polymerization is the formation of the enzyme-activated monomer. The polymerization is believed to proceed via a 'monomer-activated mechanism' [16].

Scheme 2 Reaction mechanism of the lipase catalyzed ring-opening reaction and copolymerization of ε-caprolactone with α,ω-(dihydroxy alkyl) terminated PDMS



3.1 Gel Permeation Chromatography Analysis

Results from the GPC analysis of the samples that were collected after 4½ h from the reaction mixtures of PCL/PCL–PDMS–PCL copolymers are presented in Fig. 1 and Table 1. The molecular weight build up of these copolymers – namely the weight average molecular weight (M_w), the number average molecular weight (M_n) and the polydispersity index ($PDI=M_w/M_n$) were calculated from the distributions of the chromatograms. The copolymer composition was varied by changing the concentration of the reactants [CL]/[PDMS] (80:20; 60:40; 40:60; 20:80 by w/w, respectively) in the feed mixture. Increased feed ratios of [CL]/[PDMS] resulted in an increased number average molecular weight (M_n) of the copolymers from 4,400 g mol^{-1} (20:80 w/w of [CL]/[PDMS]) to 13,950 gmol^{-1} (80:20 w/w of [CL]/[PDMS]). In other words, a decreased concentration of silicone (less initiation sites) led to an increased molecular weight, M_n of the copolymers. The synthesis of the copolymers was confirmed by the appearance of a single peak in all of the GPC chromatograms as shown in Fig. 1. Furthermore, the GPC results give support to the above reaction mechanism as presented in Scheme 1 and Scheme 2. The lipase catalyzed ring-opening polymerization of ε-caprolactone resulted in PCL homopolymer with a M_w=35,150 gmol^{-1} and a PDI=1.45.

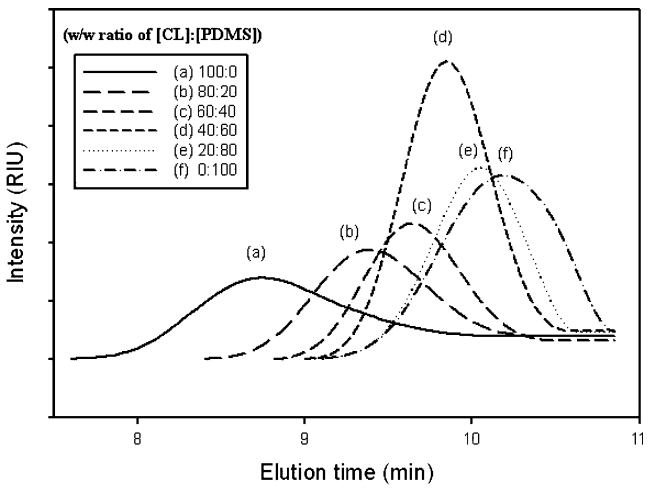


Fig. 1 Molecular weight distribution of the lipase catalyzed copolymerization of ε-caprolactone with α,ω-(dihydroxy alkyl) terminated PDMS in toluene at 70°C after 4½h as a function of the feed ratio [CL]/[PDMS]

3.2 Enzyme Recovery and Reuse

In enzymatic polymerization the recovery and reuse of the enzyme is highly desirable. The recovered immobilized lipase was washed three times with 5 ml of fresh toluene and was then reused for the synthesis of copolymers by employing the same amounts of fresh monomers under identical reaction conditions. The molecular weights of the copolymers synthesized by the recycled immobilized lipase are listed in Table 1. As one can clearly see from Table 1, the molecular weights of the copolymers synthesized using the recycled immobilized lipase were higher than the molecular weights of the copolymers synthesized using the fresh lipase, which indicates that the activity of the lipase immobilized on the acrylic resin was increased after the end of the first reaction cycle. This increased activity may be attributed to the opening up of the acrylic resin in the organic medium, which enables exposure of the lipase molecules that are otherwise buried under the surface of the resin matrix. Furthermore, the water activity in the organic medium and on the surface of the lipase is known to be critical for organic synthesis [17, 18]. The availability of water to the enzyme that is required to maintain its activity varies depending on the water partitioning among all the components of the system: the organic media, the enzyme, and the solid support [19]. Proteins are known to exhibit structural rigidity in some organic solvents and this

Table 1 Composition and molecular weight build up of the lipase catalyzed copolymerization of ε-caprolactone with α, ω-(dihydroxy alkyl) terminated PDMS in toluene at 70°C after 4½ h

[#] copolymers synthesized using lipase recovered from the first reaction cycle

[a] starting material

Sample ID	CL:PDMS w/w ratio	M_w $gmol^{-1}$	M_n $gmol^{-1}$	PDI	$^{\#}M_w$ $gmol^{-1}$	$^{\#}M_n$ $gmol^{-1}$	$^{\#}$PDI
PCL	100:0	35150	24300	1.45	61100	37750	1.62
PCL-PDMS #1	80:20	19750	13950	1.42	22400	15650	1.43
PCL-PDMS #2	60:40	12250	8650	1.42	14050	9950	1.41
PCL-PDMS #3	40:60	8700	6200	1.40	9150	6150	1.49
PCL-PDMS #4	20:80	6200	4400	1.41	6400	4700	1.36
PDMS[a]	0:100	5000	2500	2.00	–	–	–

prevents the native conformation from unfolding [20]. It is believed that water equilibration and the structural rigidity of the enzyme during the first reaction cycle may have stabilized the lipase and therefore enhanced its activity in the second reaction cycle. Moreover, at the end of the second reaction cycle, the immobilized lipase resin matrix was found to disintegrate in the solvent (toluene) used for the enzyme recovery. The activity of the enzyme was found to be reduced significantly depending on the concentration and the feed ratio of [CL]/[PDMS] in the reaction mixture (these results are not shown). Recycling experiments using the recovered lipase beyond the second cycle were therefore abandoned. The activity and stability of the immobilized lipase on this acrylic resin (N435) has been studied by several authors [21, 22]. However, in the syntheses of silicone polyesters the activity of the recovered lipase using toluene and THF were found to be reduced below 50% after 24 h of reaction time. This is apparently due to the leaching out of immobilized lipase from the acrylic resin [14].

3.3 FTIR Analysis

The FTIR spectra of the PCL−PDMS−PCL triblock copolymers were recorded by averaging 20 scans at 1 cm^{-1} resolution using a Bio-Rad Digilab Division FTS 40 IR spectrometer. FTIR spectra of all the samples were obtained from solutions prepared in toluene, except α,ω-(dihydroxy alkyl) terminated PDMS, which was recorded in the bulk state (without solvent). The characteristic peaks of the PCL and PDMS segments in the PCL−PDMS−PCL triblock copolymer are shown in Fig. 2. The absorption band at 1100 cm^{-1} is represented by the stretching vibration of Si−O bonds and the band at 1260 cm^{-1} corresponds to vibration of $Si-CH_3$ bonds of the PDMS polymer. In addition, the stretching vibration of carbonyl groups (>C=O) was seen at 1735 cm^{-1}, which was assigned to the ester structural unit in the PCL subchain. In addition, the band at 2940 cm^{-1} corresponding to (C–H) methylene was found in both the PCL and alky segment of α,ω-(dihydroxy alkyl) terminated PDMS subchains. All the above bands appeared in the FTIR spectra and indicate the presence of both PCL and PDMS subchains in the as-synthesized triblock copolymers.

3.4 Wide-angle X-ray Diffraction Analysis

Thin films of the copolymers were cast on glass plates using solutions prepared by dissolving the copolymers in THF. The solution coated glass plates were dried in a vacuum chamber at room temperature for 48 h. The crystal structure was then analyzed using wide angle X-ray diffraction.

The triblock copolymers were found to be semi-crystalline. The two main diffraction peaks, as shown in Fig. 3, appeared at 2θ values of around 21° and 23° and these are attributed to the (110) and (200) planes in PCL crystallites [23], within the PCL−PDMS−PCL triblock copolymers. Neither of the diffraction peaks changed their position upon copolymerization of PCL with PDMS. Furthermore, the half-width of both peaks were maintained, indicating that the PCL crystal sizes are similar for the copolymers when compared to the PCL homopolymer [24]. However, the intensity of the peaks is reduced with the decreased chain length of PCL in the copolymers due to the loss of total crystallinity. The degree of crystallinity, X_c(%),

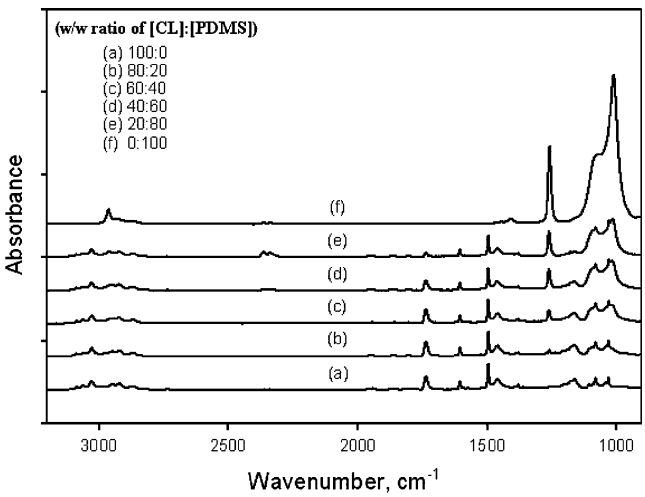


Fig. 2 FTIR spectra of the PCL−PDMS−PCL triblock copolymers as a function of the feed ratio [CL]/[PDMS]

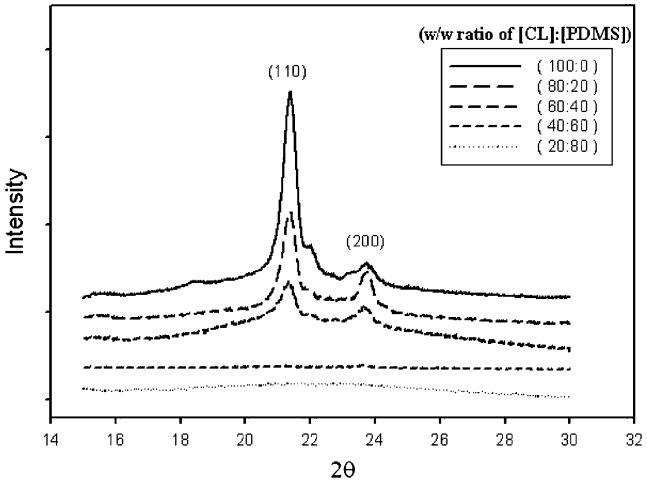


Fig. 3 Wide-angle X-ray diffraction of the PCL−PDMS−PCL triblock copolymers as a function of the feed ratio [CL]/[PDMS]

was calculated by integrating the intensity of the diffraction peaks, crystalline region, I_c (which includes the areas corresponding to both the (110) and (200) reflections in PCL), and the amorphous region, I_a using the following equation:

$$X_c(\%) = 100 \times I_c/(I_c + I_a)$$

The lipase catalyzed ring-opening polymerization of ε-caprolactone resulted in semi-crystalline PCL with a degree of crystallinity, X_c=54%. The PCL segment of the PCL−PDMS−PCL triblock copolymers retained the crystal structure and the corresponding degree of crystallinity for the samples PCL-PDMS#1, PCL-PDMS#2, PCL-PDMS#3 were 54%, 51%, 40% respectively. However, no detectable crystal peaks were observed for the sample PCL-PDMS#4. The latter sample showed a small peak in the DSC analysis, which is discussed in the following section.

3.5 Differential Scanning Calorimetry Analysis

The thermal transitions of the PCL−PDMS−PCL triblock copolymers were determined by DSC, using a TA Instruments 2010 DSC, under a nitrogen atmosphere and the DSC curves are shown in Fig. 4. Each sample was first cooled from ambient temperature to −150ºC at 10ºC /min and then heated from −150 to 100ºC at the same heating rate. From the corresponding endotherm of this last step, the glass transition temperatures (T_g) of the PCL=−65ºC and PDMS=−123ºC blocks were recorded. In addition, the melting peaks and the corresponding areas from the crystallization of PCL blocks were determined to give both melting temperature (T_m) and melting enthalpy (ΔH_m), respectively.

The values of the melting temperature, (T_m) the melting enthalpy, (ΔH_m) and the degree of crystallinity, (X_c) of all the copolymer samples are listed in Table 2. The degree of crystallinity, X_c of PCL subchains in the copolymers was estimated from the literature value for the melting enthalpy, ΔH_m of completely crystalline PCL=166 Jg^{-1} [25]. With decreasing PCL content or chain length in the copolymers, the values of ΔH_m and X_c became smaller, and the T_m shifted to lower temperatures. T_m of the PCL in the copolymers decreased up to 20 degrees compared to pure PCL. These results indicate that the crystallization behavior of PCL in these copolymers is changed. This is tentatively attributed to the decreasing chain length of the PCL in the copolymers, which reduced the number of crystallizable segments on the crystal growth front.

3.6 Thermogravimetric Analysis

The TGA curves of the PCL−PDMS−PCL triblock copolymers are presented in Fig. 5. Since both blocks are chemically bonded in the PCL−PDMS−PCL triblock copolymers, it is reasonable to assume that the unique thermal properties of the PDMS may increase the thermal stability of these copolymers relative to the PCL homopolymer. This property increased as the fraction of PDMS increased in the triblock copolymers, as can be seen in the TGA curves. For the PCL−PDMS−PCL triblock copolymers, the inflection observed in the TGA curves can be explained by assuming that a combination of free radicals results in the formation of thermally stable crosslinked products, which then decompose at higher temperatures [26, 27]. Jana et al reported an increase in the thermal stability of the blends of low-density poly(ethylene) (LDPE) and PDMS (50/50 wt %) when dicumyl peroxide was used as a crosslinker [26]. This increase was explained as a consequence of the introduction of cross-

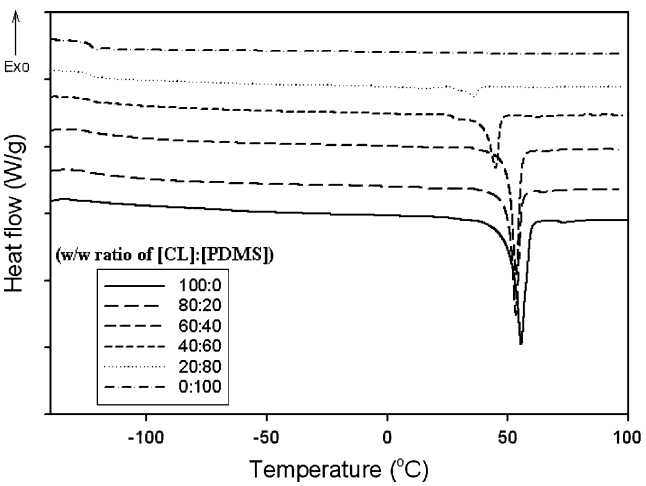


Fig. 4 DSC curves of the PCL−PDMS−PCL triblock copolymers as a function of the feed ratio [CL]/[PDMS]

Table 2 Degree of crystallinity, melting temperature and melting enthalpy of the PCL−PDMS −PCL triblock copolymers

Sample ID	CL:PDMS w/w ratio	T_m (ºC)	ΔH (Jg^{-1})	$X_c(\%)^{\#a}$	$X_c(\%)^{\#b}$
PCL	100:0	55.5	94.8	57	54
PCL-PDMS #1	80:20	55.0	72.3	54	54
PCL-PDMS #2	60:40	53.5	53.0	53	51
PCL-PDMS #3	40:60	45.0	31.9	47	40
PCL-PDMS #4	20:80	35.0	15.4	45	–
PDMS	0:100	–	–	–	–

[#] Degree of crystallinity calculated from the DSC[a] and WAXD[b] data, respectively and the values were corrected for copolymer composition

links at the interface as well as the formation of inter- and intramolecular crosslinking in the bulk of the matrix [27].

Furthermore, Clarson and Semlyen reported the onset temperature of weight loss for linear PDMS was at 360ºC and essentially 100% weight loss was achieved by 580ºC [28]. A residue of about 0.3% of the PDMS remained after heating under nitrogen and 62% of the residue was found as a thermally inert white powder after heating under oxidative conditions in oxygen. The onset of an exothermic process in oxygen was observed at 260ºC, which attained a maximum rate at 325ºC. This was proposed to be associated with the oxidative crosslinking via the methyl groups typically observed for high molar mass linear PDMS. Persenaire et al. reported that thermal degradation of PCL proceeds by a two-stage mechanism occurring at different temperatures. At temperatures below 300 °C, an ester pyrolysis reaction produces gases consisting of H_2O, CO_2, and 5-hexenoic acid. At higher temperatures, PCL depolymerizes *via* an unzipping mechanism which requires the presence of hydroxyl end groups and this leads to the formation of ε-caprolactone [29].

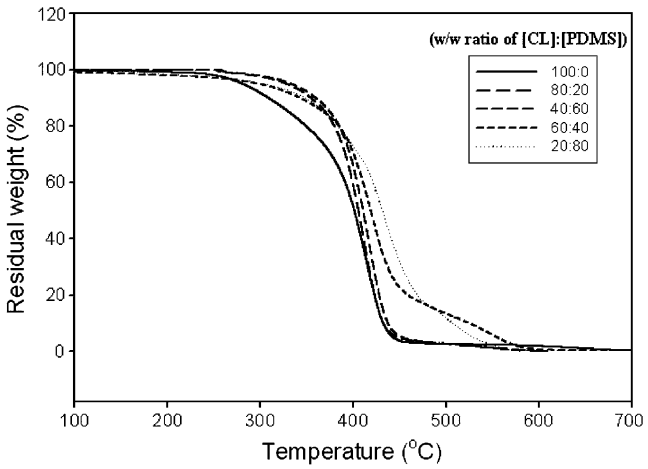


Fig. 5 TGA curves of the PCL−PDMS−PCL triblock copolymers as a function of the monomer feed ratio [CL]/[PDMS], heated under nitrogen.

4 Conclusions

PCL is a biodegradable, non-toxic, biocompatible and water insoluble polymer which is suitable for controlled drug delivery due to its high permeability for many drug molecules. It also has the ability to form compatible blends with other polymer systems. Biodegradation of PCL is very slow in comparison to other polymers, thus it is suitable for long-term drug delivery extending over a period of more than one year. PCL is a semi-crystalline polymer having a glass transition temperature around −60ºC and melting point in the range 59 to 64ºC, depending upon its crystalline nature and thermal history [6].

Block copolymers are an important class of polymeric materials due to their ability to self-assemble into supramolecular structures, either in the bulk or in selective solvents. Among them, the block copolymers incorporating PDMS represent a special category, owing to their particular properties: excellent thermal and oxidative stability, high chain flexibility, low glass transition temperature, biocompatibility, low surface energy, low solubility parameter and an ability of the siloxane segments to "surface segregate" [30].

In the present work, PCL−PDMS−PCL triblock copolymers were enzymatically synthesized using immobilized lipase B from *Candida antarctica* as a catalyst. The copolymers were found by DSC and XRD to be semi-crystalline and the degree of crystallinity increased with an increase of the feed ratio [CL]/[PDMS]. The crystal structure of the copolymers determined from WAXD was found to be similar to that of the PCL homopolymer. The thermal stability of these copolymers improved over the PCL homopolymer with increased fraction of PDMS as shown by TGA.

The recycled lipase gave higher molecular weight copolymers, apparently due to an increased activity of the lipase following an opening up of the immobilized acrylic resin matrix in the organic medium. Proteins are known to exhibit structural rigidity in some organic solvents and this prevents the native conformation from unfolding [20]. It is believed that water equilibration and the structural rigidity of the enzyme during the first reaction cycle may have

stabilized the lipase and therefore enhanced its activity in the second reaction cycle. However, subsequent recycling of the lipase was hindered due to a complete disintegration of the acrylic resin matrix.

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