Microblock Copolymers as a Result of Transesterification Catalyzing Behavior of Lipase CA in Sequential ROP

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Received January 16, 2007; Revised Manuscript Received March 15, 2007

ABSTRACT: The copolymerization of ϵ-caprolactone (CL) and 1,5-dioxepan-2-one (DXO) was performed by sequential addition of monomers in lipase CA catalyzed ring-opening polymerization (ROP) at 60 °C in bulk. CL was first polymerized up to a monomer conversion of 95%, and then DXO was added to the reaction mixture. The polymerization was stopped when the DXO conversion reached a level of more than 95%. The molar feed ratio of CL and DXO was varied from 1.5 to 10, and the copolymer composition, as determined by ^{1}H NMR spectroscopy, agreed well with the feed. The block lengths of PCL and PDXO segments in the structure of these high molecular weight copolymers reduced significantly due to the occurrence of extensive transesterification during ROP. The enzyme, lipase CA, in addition to acting as the catalyst for ROP also promoted transesterification reactions. The increase in number-average molecular weight (M_n) after DXO polymerization in the second step illustrated that the terminal hydroxyl group of preformed PCL chains in the first step possibly initiated the DXO polymerization. A single glass transition, in between the glass transition temperatures of corresponding homopolymers of PDXO and PCL, was observed in the DSC thermograms of all the copolymers. A composition of 15−20% DXO gave optimal balance between strength and elasticity of the copolymers.

Introduction

High selectivity, mild polymerization conditions, no toxicity, and recyclability of enzymes has resulted into increased research interest to use them as catalysts for ring-opening polymerization (ROP).[1] Because of enzyme's origin from natural sources, they have been taken as substitute for the toxic organometallic catalysts to polymerize various lactones and lactides, resulting in aliphatic polyesters suitable for biomedical and pharmaceutical applications. Lipase CA (*Candida antarctica*), for example, has been widely recognized as a versatile catalyst for ROP, and homopolymers from different lactones and lactides have been successfully synthesized using this enzyme.[1−3]

As a next step in the progress of this field, the effectiveness of enzymes to synthesize various macromolecular architectures is the widely researched topic of today. Recently, the scope of lipase CA has been further widened by the synthesis of random, block, or graft copolymers. Copolymers are of particular interest because the properties of two or more monomers can be combined in a single polymer which can be tailored and utilized in an advantageous manner. Random copolymers of ϵ-caprolactone (CL) with β-propiolactone (PL),[4] 8-octanolide (OL),[5] 12-dodecanolide (DDL),[5] ω-pentadecalactone (PDL),[6] γ-butyrolactone (BL),[7] or 1,5-dioxepan-2-one (DXO)[8] have been synthesized using lipase-catalyzed ROP. With the use of dihydroxy-terminated poly(ϵ-caprolactone) to initiate DXO polymerization, a triblock-like architecture was obtained; however, the polydispersity of the copolymers was high due to transesterification reactions.[9] 2-Oxo-12-crown-4 ether was polymerized with PDL using lipase CA, and a random copolymer was obtained.[10] Two different modes of polymerization, i.e., lipase-catalyzed ROP and polycondensation, were used to perform one-pot synthesis of copolyesters from lactones, dicarboxylic acid divinyl esters, and glycols.[11] A combination of enzyme-catalyzed ROP and atom transfer radical polymerization (ATRP) from a bifunctional initiator has been reported recently to synthesize block copolymers of CL with styrene,[12−14] methyl methacrylate,[15−19] *tert*-butyl methacrylate,[18] or 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate.[20] Block copolymers of CL or 4-methyl-ϵ-caprolactone with styrene have also been formed by combining enzyme-catalyzed ROP and nitroxide-mediated free-radical polymerization using a bifunctional initiator.[21] Similarly, simultaneous enzymatic ROP and reversible addition−fragmentation chain transfer (RAFT)-mediated polymerization of CL and styrene using hydroxyl-terminated trithiocarbonate resulted in formation of block copolymers.[22] Random copolymers of trimethylene carbonate (TMC) have also been synthesized with 5-methyl-5-benzyloxycarbonyl-1,3-dioxan-2-one (MBC),[23] PDL,[24] or 5-methyl-5-carboxyl-1,3-dioxan-2-one (MCC)[25] using lipase-catalyzed ROP.

As described in the literature cited above, the synthesis of block copolymers with the use of enzymes was possible by combining ATRP, RAFT, or nitoxide-mediated free radical polymerizations of vinyl monomers with enzyme-catalyzed ROP of lactones. With the involvement of metal-based catalysts in ATRP, the polymers obtained thereof may become unsuitable for biomedical or pharmaceutical applications. Moreover, in contrast to the copolymers involving vinyl monomers, our purpose was to make biocompatible and degradable polymers. The overall objective of this article was to use enzyme for sequential ROP of lactones to obtain a biocompatible, degradable polymer without metallic impurities. The copolymerization of CL and DXO was performed for this purpose by sequential addition of monomers in lipase CA-catalyzed ROP at 60 °C in bulk. We also aimed to study the effect of lipase CA's transesterification catalyzing behavior on the structure of the copolymer in sequential copolymerization and to appraise the feasibility of formation of blocklike architecture of the copolymer under these conditions.

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10.1021/ma0701179 CCC: $37.00 © 2007 American Chemical Society
Published on Web 06/05/2007

Experimental Section

Materials. Tetrahydro-4*H*-pyran-4-one (98%, Maybridge Chemical, UK), *m*-chloroperoxybenzoic acid (70−75%, balance 3-chlorobenzoic acid and water, Acros, Belgium), dichloromethane, $MgSO_4$ (99.5%), $NaHSO_3$ (minimum 99%), $NaHCO_3$ (99%), and diethyl ether (analytical grade solvents, Labora, Sweden) were used as received. ϵ-Caprolactone (99%, Aldrich, Germany) was dried and distilled over CaH_2 at reduced pressure prior to use. Novozyme 435 (activity ∼10 000 PLU/g according to the supplier) was donated by Novozyme Inc., Denmark. Novozyme 435 (lipase CA) is a lipase (B lipase) from *Candida antarctica* produced by submerged fermentation of a genetically modified *Aspergillus oryzae* microorganism absorbed on a microporous resin. It consists of bead-shaped particles with a diameter in the range of 0.3−0.9 mm. The bulk density of Novozyme 435 is ∼0.43 g/cm^3, and it has a moisture content of 1−2% w/w. DXO was synthesized in the laboratory.

Synthesis of 1,5-Dioxepan-2-one (DXO). The DXO was synthesized from tetrahydro-4*H*-pyran-4-one through Baeyer−Villiger oxidation according to the method reported by Mathisen et al.[26] The DXO obtained was purified by recrystallization from diethyl ether and two subsequent distillations under reduced pressure. Finally, the monomer was dried over CaH_2 overnight and distilled under reduced pressure. ^{1}H NMR δ (ppm): 4.2 (t, 2H, $-CH_2-O-CO-$), 3.8 (t, 2H, $-CH_2-CH_2-O-CO-$), 3.7 (t, 2H, $-CH_2-CH_2-CO-O-$), 2.6 (t, 2H, $-CH_2-CO-O-$).

Synthesis of Copolymers. In a typical polymerization, 4.0 g of CL (0.035 mol) and enzyme (5.0 wt % of the monomer) were weighed in a round-bottom flask, having fittings for nitrogen purging, inside the glovebox. The flask was then immersed in an oil bath at 60 °C under continuous mechanical stirring for 12 h in a nitrogen atmosphere. The second monomer, DXO (0.004−0.023 mol), was added to the reaction mixture after 12 h when more than 95% CL had been converted. The system was allowed to stir at 60 °C until DXO conversion has reached a level of more than 95%. This took from 1 to 2 h, depending upon the DXO amount. The flask was then removed from the oil bath, and the polymer was isolated by dissolving the reaction mixture in chloroform and removal of enzyme by filtration followed by precipitation in excess cold hexane. The polymer was dried under vacuum before analysis. Copolymers having different molar feed ratio of CL and DXO were synthesized by varying the amount of DXO (0.004−0.023 mol) in the feed.

Characterization. NMR. The monomer conversion and the copolymer composition were determined by ^{1}H NMR spectroscopy, and the monomer sequence in copolymers was evaluated using ^{13}C NMR spectroscopy. A Bruker Avance 400 MHz NMR instrument operating at 400.13 and 100.62 MHz for ^{1}H and ^{13}C, respectively, was used for this purpose. $CDCl_3$ was used as solvent as well as internal standard ($\delta = 7.26$ and 77.0 ppm).

SEC. The molecular weight of the polymers was determined by size exclusion chromatography (SEC) using dimethylformamide (DMF) as eluent at a flow rate of 1.0 mL/min. The injection volume was 50 μL. A Waters 717 plus autosampler and a Waters model M-6000A solvent pump equipped with a PL-EMD 960 light scattering evaporative detector, two PL gel 10 μm mixed-B columns (300 × 7.5 mm) from Polymer Laboratories, and one Ultrahydrogel linear column (300 × 7.8 mm) from Waters connected to an IBM-compatible PC were used. The two PLgel 10 μm mixed-B columns can separate a molecular weight range of 500−10 000 000, while the Ultrahydrogel linear column can separate a molecular weight range of 1000−7 000 000 and it has a pore size of 120−2000 Å. The PL-EMD LS detector has a light source of multiwavelength visible (halogen bulb with tungsten filament), power requirements of 110V/60 Hz or 230V/50 Hz, and the temperature range of 30−200 °C. The temperature was 120 °C during analysis of these polymer samples. Narrow molecular weight polystyrene standards were used for calibration. Millenium version 3.20 software was used to process the data.

DSC. The thermal properties of the polymers were determined by differential scanning calorimetry (DSC) using a Mettler-Toledo DSC 820 module under a nitrogen atmosphere (nitrogen flow rate 80 mL/min) with a sample mass of 5 ± 1 mg and a heating rate of 5 °C/min. The samples were subjected to a heating−cooling−heating cycle from −70 to 100 °C, and the analysis was performed on the second heating plot. The DSC instrument was calibrated against the onset melting temperature and enthalpy of fusion of pure Indium. The glass-transition temperature (T_g) was measured as the midpoint of the shift in the baseline while the melting temperature (T_m) was taken as the endothermic peak maximum.

The relative crystallinity of the PCL segment of different samples was calculated according to eq 1:

$$w_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \qquad (1)$$

where w_c is the crystallinity, ΔH_f is the heat of fusion of the sample, and ΔH_f^0 is the heat of fusion of 100% crystalline PCL. The value of ΔH_f^0 used for the calculations was 139.5 J/g.[27]

Tensile Testing. Tensile testing of the polymer films prepared by solution casting was performed on an Instron 5566 equipped with pneumatic grips and controlled by a Dell 466/ME personal computer. The tensile measurements were made with a cross-head speed of 50 mm/min and an initial grip separation of 32 mm. The samples had dimensions of 80 × 5 mm and a thickness of ∼0.5 mm. The average thickness of each sample was calculated from five independent measurements with a Mitutoyo micrometer. The samples were preconditioned for 48 h at 50 ± 5% RH and 23 ± 1 °C. Five different samples from the same polymer film were tested in accordance with ASTM D882-95A.

DMTA. Dynamic mechanical properties of the copolymers were determined using TA Instruments DMTA Q800. The measurements were made in the tensile mode with a distance of 12.86 mm between the grips. The temperature for measurement was programmed from −80 to 40 °C at a rate of 3 °C/min. The measurements were performed at 1 Hz, and a static force of 1 N was applied. The width of the samples was 5 mm, and the average sample thickness, as determined from five independent measurements using Mitutoyo micrometer, was 0.3 mm.

Results and Discussion

The environment friendly characteristic is the most advantageous feature of enzymes for their use as catalyst in ROP besides their strict control on stereo- and regioselectivity of the reactants. On the other hand, the use of enzymes has its own disadvantages such as high cost, large quantity of enzymes required for polymerization, and often formation of low molecular weight products. The use of enzymes, especially lipase CA, has been explored to synthesize homopolymers from various lactones, although the synthesis of block copolymers was possible with incorporation of vinyl monomers using techniques such as ATRP or RAFT. In this work we accessed the effectiveness of lipase CA in retaining its capacity to further catalyze the ROP, from a preformed polymer chain, whenever additional monomer is supplied and also the feasibility of formation of blocklike architecture of the copolymer under these conditions.

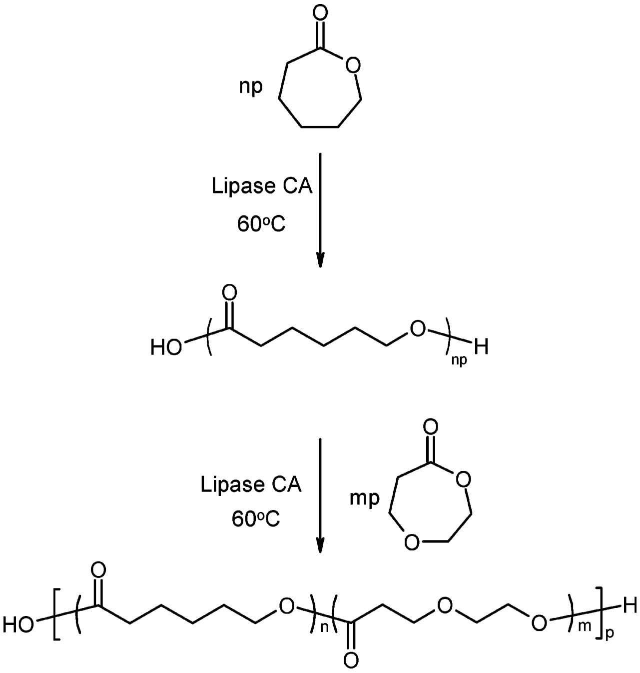
Sequential Addition of CL and DXO in Lipase CA-Catalyzed ROP. Lipase CA (Novozyme 435) has a high polymerization activity for lactones, it can be easily removed from the final product by filtration, and it does not release any toxic metallic residues. When it was used as a catalyst for ROP in bulk at 60 °C, the reaction system could be described as a suspension of enzyme beads in the monomer, and an increase in viscosity was observed with time. In our earlier publication, we have reported the synthesis of copolymers based on DXO and CL by lipase CA-catalyzed simultaneous copolymerization at 60 °C in bulk.[8] The DXO was found to be more reactive than CL under lipase CA catalysis.[8,28] In this work, the

Table 1. Copolymers of CL and DXO Synthesized by Sequential Addition of Monomers in Lipase CA-Catalyzed ROP in Bulk at 60 °C

	feed composition (mol %)				polymer composition[b] (mol %)			block length[c]					
polymer	CL	DXO	molar ratio	yield[a] (%)	CL	DXO	molar ratio	CL	DXO	M_n[d]	PDI[d]	M_n[e]	PDI[e]
1	60.0	40.0	1.5	74.8	61.7	38.3	1.6	2.80	1.75	31 000	1.5	53 100	1.5
2	75.0	25.0	3.0	74.3	74.9	25.1	3.0	4.69	1.61	31 000	1.5	50 200	1.4
3	79.8	20.2	4.0	75.6	80.9	19.1	4.2	5.72	1.39	31 000	1.5	49 400	1.5
4	83.4	16.6	5.0	80.3	84.0	16.0	5.2	7.56	1.33	31 000	1.5	48 000	1.4
5	87.5	12.5	7.0	79.5	87.9	12.1	7.3	9.91	1.22	31 000	1.5	43 000	1.4
6	90.9	9.1	10.0	81.5	91.0	9.0	10.1	11.8	1.19	31 000	1.5	37 300	1.5

[a] Determined by gravimetric analysis. [b] Determined by ^{1}H NMR analysis of the precipitated polymer. [c] Determined by ^{13}C NMR analysis of the precipitated polymer. [d] Average molecular weight and PDI (from the six polymerizations) of PCL synthesized in first step, determined by SEC analysis using polystyrene standards. [e] Molecular weight of copolymer after DXO polymerization in the second step, determined by SEC analysis using polystyrene standards.

Scheme 1. Sequential Addition of CL and DXO in Lipase CA-Catalyzed ROP



copolymers were synthesized by sequential addition of monomers CL and DXO. This was done in order to assess the effectiveness of lipase CA for sequential one-pot polymerization process and also to study its effect on the extent of transesterification reactions occurred during the ROP. CL was first polymerized with lipase CA at 60 °C in bulk, and after it reached a monomer conversion level of more than 95%, DXO was added to the reaction mixture. The polymerization was stopped when more than 95% DXO had been converted. The reaction scheme is shown in Scheme 1. There were several reasons for polymerizing CL before DXO. PDXO is an amorphous, waxy, and expensive polymer lacking mechanical strength, and it was therefore required in small amounts to improve the hydrophilicity and degradability of PCL. If such a small amount of DXO were to be polymerized with the same amount of enzyme as was used with CL (5 wt % of 4.0 g of CL), a large number of polymer chains with very low DP would be generated. On the other hand, if a small amount of enzyme were to be used to compensate for this result, it would take much longer time for monomers, especially CL, to polymerize and the extent of transesterification would be higher.

The molar feed ratio of monomers (CL/DXO) was varied from 1.5 to 10 as shown in Table 1. The monomer conversion was determined from ^{1}H NMR spectra of crude reaction mixture by taking the ratio of peak intensities due to polymer and monomer. For CL, the ratio of the intensities of oxymethylene protons of PCL at ~4.0 ppm (t, 2H, $-CH_2-O-CO-$) and CL at ~4.1 ppm (t, 2H, $-CH_2-O-CO-$) was used to calculate the percentage monomer conversion. Once the CL conversion reached 95%, DXO was added to the reaction mixture and the monomer conversion for DXO was obtained by comparing the peak intensities of oxymethylene protons at ~4.1 ppm (t, 2H, $-CH_2-O-CO-$) due to PDXO and at ~4.2 ppm (t, 2H, $-CH_2-O-CO-$) due to DXO. The polymerization was stopped when more than 95% DXO had been polymerized.

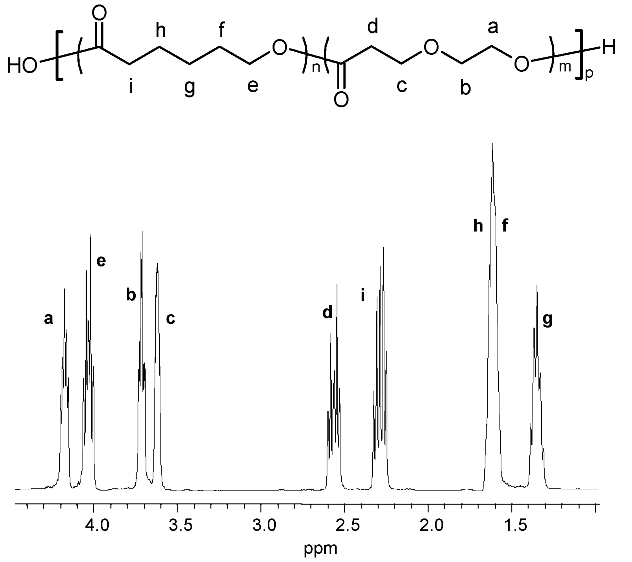


Figure 1. ^{1}H NMR spectrum of CL- and DXO-based copolymer synthesized by sequential addition of monomers in lipase CA-catalyzed ROP in bulk at 60 °C.

The polymer composition was calculated from the ^{1}H NMR spectra of precipitated polymer, using the ratio of peak intensities due to PCL at ~4.0 ppm and PDXO at ~4.1 ppm. A typical ^{1}H NMR spectrum of copolymer is shown in Figure 1. The feed and the polymer composition agreed very well as shown in Table 1, in contrast to the situation when both CL and DXO were polymerized together and a lower CL/DXO molar ratio was observed in the copolymers than in the feed.[8] The reason assigned for the lower CL/DXO molar ratio was the higher reactivity of DXO than CL toward lipase CA catalysis. To evaluate the microstructure of the synthesized copolymers, sequence analysis was carried out in the carbonyl region of ^{13}C NMR spectra due to its greater sensitivity to sequence effects than ^{1}H NMR.[29] The ^{13}C NMR spectra of the copolymers are shown in Figure 2. Four different peaks corresponding to the homopolymers and two dyads, i.e., transitions between CL (C) and DXO (D) and vice versa, are assigned in the spectrum. The spectra revealed that extensive transesterification reactions occurred during the lipase CA-catalyzed ROP which resulted in microblock formation. The peak at 173.4 ppm due to the

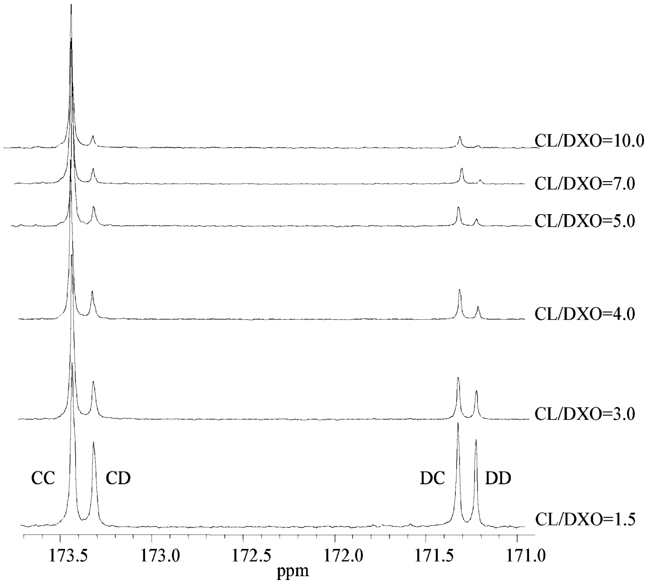


Figure 2. ^{13}C NMR spectra of CL- and DXO-based copolymers synthesized by sequential addition of monomers in lipase CA-catalyzed ROP in bulk at 60 °C; variation of block length with CL/DXO molar feed ratio.

CL−CL (CC) sequence increased while the peak at 171.2 ppm due to the DXO−DXO (DD) sequence decreased, as the CL/DXO molar feed ratio was increased (Figure 2). The average block lengths of PCL ($\bar{L}_{\rm CL}$) and PDXO ($\bar{L}_{\rm DXO}$) sequences were calculated from the intensity (I) of carbonyl signals using eqs 2 and 3, respectively.

$$\bar{L}_{\rm CL} = \frac{I_{\rm CC}}{I_{\rm CD}} + 1 \tag{2}$$

$$\bar{L}_{\rm DXO} = \frac{I_{\rm DD}}{I_{\rm DC}} + 1 \tag{3}$$

Although the average block length of PCL and PDXO was higher than the values obtained before upon simultaneous copolymerization of CL and DXO,[8] the extensive transesterification reactions resulted into more random arrangement of monomer units and copolymers having microblock structure. An increase in PCL block length and a decrease in PDXO block length were observed when the CL/DXO molar feed ratio was increased from 1.5 to 10 (Table 1).

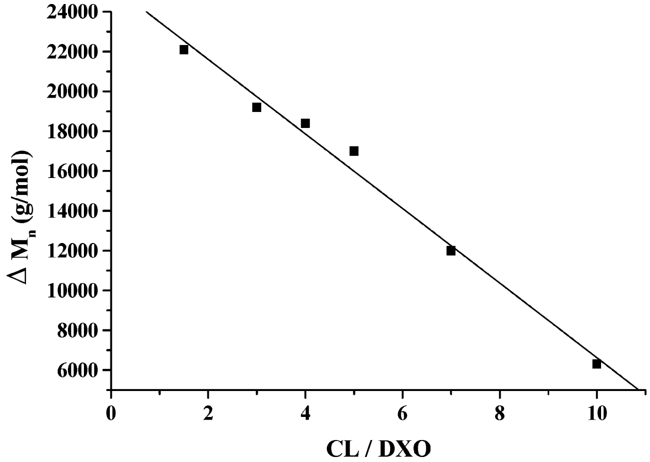


Figure 3. Increase in $M_{\rm n}$ ($\Delta M_{\rm n}$, from 31 000 g/mol of PCL formed in the first step) due to DXO polymerization in the second step of sequential copolymerization of CL and DXO using lipase CA at 60 °C in bulk.

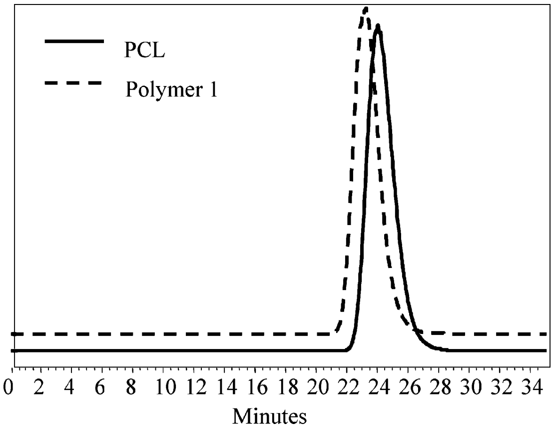


Figure 4. SEC chromatograms of PCL synthesized in the first step and its copolymer with DXO (polymer 1) synthesized in the second step of lipase CA-catalyzed sequential copolymerization of CL and DXO at 60 °C in bulk.

The molecular weight of the polymers was obtained from SEC using polystyrene standards, and the values of number-average molecular weight ($M_{\rm n}$) and polydispersity index (PDI) are shown in Table 1. The $M_{\rm n}$ values of PCL synthesized in the first step of all the six polymerizations were close to 31 000 g/mol with PDI values ranging from 1.53 to 1.56. This confirmed the repeatability of the process, and in Table 1 the average value of $M_{\rm n}$, i.e., 31 000 g/mol, is therefore reported. After complete polymerization of the DXO, added in the second step of polymerization, the molecular weight was found to increase in all the reactions as shown in Table 1. The increase in $M_{\rm n}$ ($\Delta M_{\rm n}$, after DXO polymerization in the second step) with increasing proportion of DXO in the feed followed a linear trend, as shown in Figure 3. This showed that the DXO added in second step was indeed getting attached to the preformed PCL chains in the reaction mixture. This was also shown by comparing the SEC chromatograms of PCL synthesized in the first step and the copolymer of CL and DXO obtained after addition of DXO in the second step. As shown in Figure 4, a single peak at a shorter retention time than that given by PCL was observed after DXO polymerization in the second step. This result suggested that the DXO polymerization in the second step was possibly initiated by the terminal hydroxyl group of the preformed PCL chains. However, extensive transesterification reactions during ROP led to microblock structure in the final copolymers.

Kobayashi et al. have shown the ROP of 12-dodecanolide or 15-pentadecanolide using lipase PF in the presence of PCL having $M_{\rm n} = 1.9 \times 10^4$ g/mol.[30] They observed that the molecular weight as determined from the SEC chromatograms first decreased and then started increasing; however, the values were never higher than the initial $M_{\rm n}$ value for PCL. The decrease in $M_{\rm n}$ was assigned to the hydrolytic degradation of the PCL, and later on the increase in $M_{\rm n}$ occurred due to the polymerization of the added lactone along with parallel transesterification reactions. The value of $M_{\rm n}$ (12.5×10^3 or 9.6×10^3 g/mol) of the copolymer synthesized in this way was lower than the initial $M_{\rm n}$ of the PCL even after 98% conversion of the lactone monomer. In our results the $M_{\rm n}$ values increased, as compared to the preformed PCL chains, when DXO was polymerized in the second step. This showed that no significant hydrolytic degradation of PCL chains, formed in first step of polymerization, has occurred. The PDI values of the copolymers remained unchanged or even decreased in some cases as shown in Table 1. The decrease in PDI suggested that the short PCL

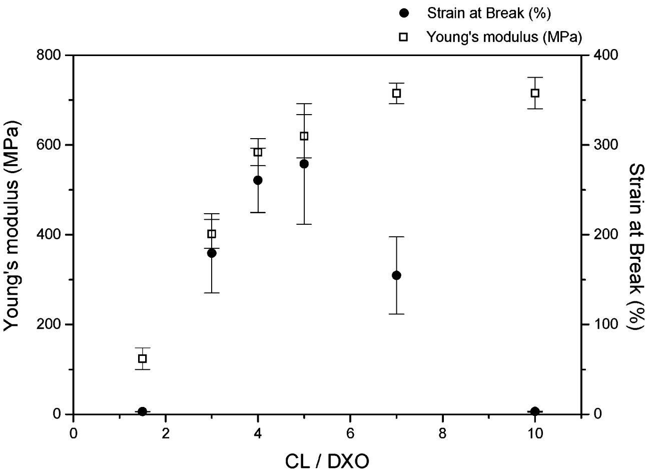


Figure 5. Tensile properties of copolymers synthesized via lipase CA-catalyzed sequential copolymerization of CL and DXO at 60 °C in bulk.

Table 2. Thermal Properties of Copolymers of CL and DXO Synthesized by Sequential Addition of Monomers in Lipase CA-Catalyzed ROP in Bulk at 60 °C

polymer	T_g (°C)	T_m (°C)	W_c (%)
1	−53.4	25.8	24.5
2	−56.3	43.7	26.2
3	−58.6	45.2	34.8
4	−59.7	48.9	36.5
5	−61.3	50.4	38.2
6	−62.3	51.8	40.4

chains, due to their high diffusivity in a bulk polymerization system, had high accessibility to initiate the DXO polymerization so that the dispersity of the chains decreased when more DXO molecules were attached to short PCL chains.

Thermal Properties. PDXO is an amorphous polymer having glass transition temperature (T_g) at 39 °C whereas PCL is a semicrystalline polymer having T_g and melting temperature (T_m) close to −65 and 60 °C, respectively. A single glass transition, in between the glass transition temperatures of the homopolymers of PDXO and PCL, was observed in the DSC thermograms of all the copolymers. This was again the result of extensive transesterification occurred during lipase CA-catalyzed ROP. The T_g values, shown in Table 2, increased linearly with increasing the DXO content of the copolymers. The PCL segment of the copolymer showed a tendency to crystallize, as revealed by the presence of a melting peak in the DSC thermograms. The T_m decreased with increasing DXO content of the copolymers due to the formation of smaller and less perfect crystals by shortening of PCL crystalline segments (Table 2). The relative crystallinity (w_c) of the PCL segment was calculated from the heat of fusion (H_f) of different copolymers in comparison to the heat of fusion of 100% crystalline PCL (H_f^0). Because of the hindrance created by PDXO domains in the crystallization of PCL blocks, the crystallinity of PCL segments of the copolymers, given in Table 2, decreased with increasing DXO content in the copolymers.

Tensile Properties. The copolymers showed a single T_g in the DSC thermograms indicating one amorphous phase and a crystalline domain of PCL segments. These soft-amorphous and hard-crystalline parts intertwined through chain segments incorporated in both domains could introduce thermoplastic elstomeric behavior. The tensile properties were thus expected to depend upon copolymer composition. The results of the tensile tests are shown in Figure 5. A higher DXO content reduced the Young's modulus of the copolymers, indicating that it acted as a plasticizer. In copolymers of DXO and CL synthesized by our group using Sn-based catalyst the strain at break showed a tendency to increase with increasing molecular weight or increasing DXO content.[31] As shown in Figure 5, the strain at break increased with decreasing CL/DXO molar feed ratio from 10 to 5, following the similar trend. A further decrease in CL/DXO molar feed ratio resulted in a decrease in the strain at break, and it was found that a composition of 15−20% DXO gave an optimal balance between strength and elasticity of the copolymers.

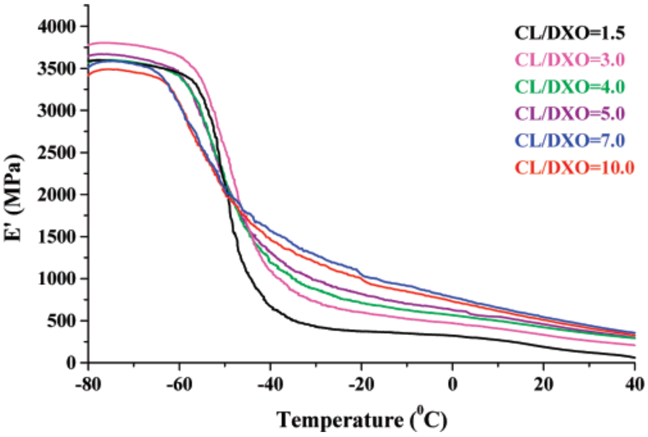


Figure 6. Storage modulus E' vs temperature for copolymers synthesized via lipase CA-catalyzed sequential copolymerization of CL and DXO at 60 °C in bulk.

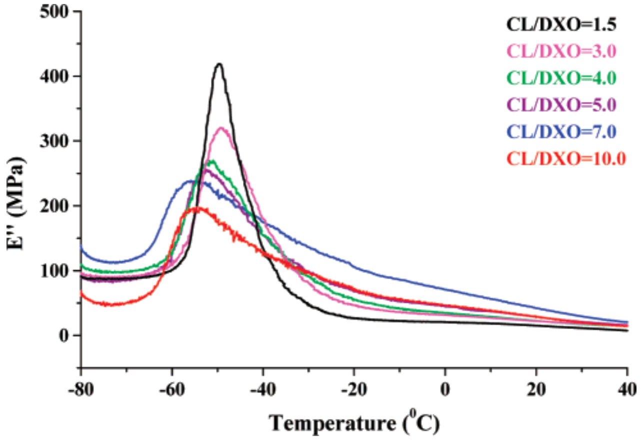


Figure 7. Loss modulus E'' vs temperature for copolymers synthesized via lipase CA-catalyzed sequential copolymerization of CL and DXO at 60 °C in bulk.

DMTA. As shown in Figure 6, the copolymers showed a sharp drop in the storage modulus (E') in the temperature region corresponding to the glass transition, which confirmed the results of the DSC analysis. The loss modulus (E'') value, as shown in Figure 7, increased with increasing DXO content of the copolymers. A shift toward lower temperature was also observed for the temperature associated with E'' peak with increasing PCL content. All the samples exhibited one sharp tan δ peak (Figure 8), and with increasing DXO content of the copolymers, the peak value of tan δ increased. This indicated a greater relaxation strength due to large fraction of less constrained chains participating in the relaxation process. A high DXO content gave a large fraction of chain segments which were less constrained by the PCL crystalline domains, and therefore more mobile chain segments increased the relaxation strength.

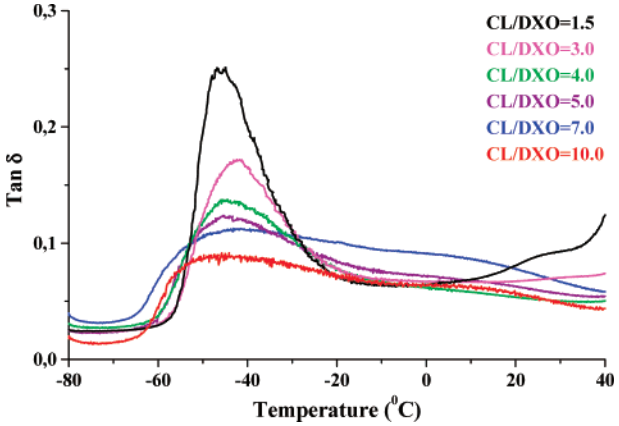


Figure 8. Loss factor (tan δ) vs temperature for copolymers synthesized via lipase CA-catalyzed sequential copolymerization of CL and DXO at 60 °C in bulk.

Conclusions

Lipase CA, being an effective catalyst for ring-opening polymerization on one hand, also promoted transesterification reactions during the sequential copolymerization of CL and DXO in bulk at 60 °C. As a result, the architecture of the CL- and DXO-based copolymers was altered into a more random arrangement of monomer units in the polymer chains and the copolymers had microblock structure. The increase in M_n with the supply of additional monomer (DXO) in the second step illustrated that the terminal hydroxyl group of preformed PCL chains in the first step, possibly initiated the DXO polymerization and the additional monomer was getting attached to the preformed chains. The copolymer composition matched very well with the feed and the block lengths of the two monomers varied with their molar feed ratio. A single glass transition temperature confirmed the microblock structure of the copolymers obtained as a result of extensive transesterification reactions occurred during ring-opening polymerization. A variation in feed composition resulted into high molecular weight copolymers having tunable mechanical properties and copolymer containing 15−20% DXO showed optimal balance of the tensile properties.

Acknowledgment. The authors thank SSF (The Swedish Foundation for Strategic Research), STINT (The Swedish Foundation for International Cooperation in Research and Education), and The Royal Institute of Technology for financial support of this work.

References and Notes

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MA0701179