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Living Ring-Opening (Co)polymerization of 6,7-Dihydro-2(5*H*)-oxepinone into Unsaturated Aliphatic Polyesters

X. Lou, C. Detrembleur, Ph. Lecomte, and R. Jérôme*

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium

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ABSTRACT: Homopolymerization of the unsaturated cyclic ester, 6,7-dihydro-2(5*H*)-oxepinone (DHO), and copolymerization with ϵ-caprolactone (ϵCL) are an easy way to produce unsaturated aliphatic polyesters in a controlled manner. Polymerization of DHO initiated by $Al(O^{i}Pr)_3$ in toluene at room temperature proceeds by a coordination−insertion mechanism and is living as certified by the agreement between the experimental molecular weight at total monomer conversion and the value predicted from the initial monomer to initiator molar ratio. The polydispersity is also low ($M_w/M_n \leq 1.2$). Random copolymerization of DHO and ϵCL leads to the same conclusion. Beyond the complete monomer conversion, the poly(DHO) chains experience mainly intermolecular transesterification reactions at the same rate as poly(ϵCL) under the same conditions. The livingness of the ROP of both DHO and ϵCL allows diblock copolymers to be synthesized with predicted composition and molecular weight. Homopoly(DHO) is semicrystalline with T_m at 35 °C and T_g at −50 °C. T_m and thermal stability can be modulated by copolymerization of DHO with ϵCL.

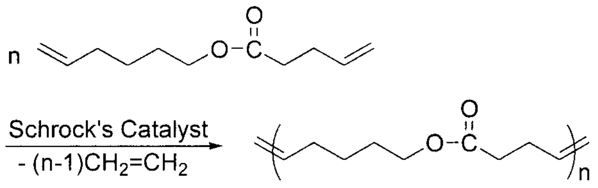
Introduction

Polycondensation of glycols with dibasic acid, diesters, or dianhydrides at elevated temperature is a conventional method to prepare both saturated and unsaturated polyesters.[1] These polymers are commonly available in a range of rather low number-average molecular weights (15 000−20 000), which makes their processing by molding or coating quite easy.

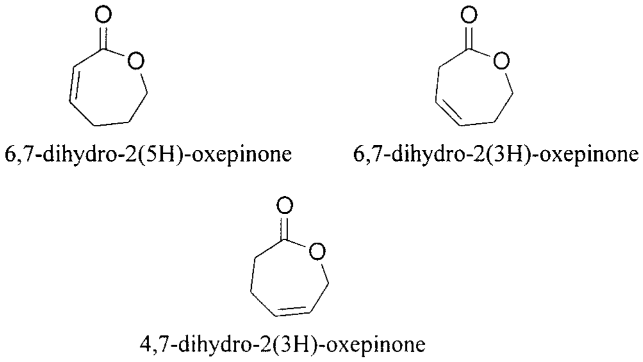
Acyclic diene metathesis (ADMET) polymerization is a better route to linear unsaturated polyesters. Wagener et al.[2] studied the ADMET polymerization of 1-hexenyl 1-pentenoate using Schrock's molybdenum catalyst, $Mo(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$ (R = Me, Ph). They accordingly prepared unsaturated aliphatic polyesters end-capped by vinyl group (Scheme 1). The polymerizability of this type of monomer is limited by the number of methylene units between the double bond and the ester functionality. Moreover, ADMET polymerization is also a polycondensation reaction which is limited to low molecular weight (<15 000) and broad molecular weight distribution.

Substantial progress in the control of ring-opening polymerizations (ROP) of lactones, lactides, and glycolide has been reported for the past decades. The use of aluminum alkoxides with or without functional groups has largely contributed to the controlled synthesis of aliphatic polyesters, including functional oligomers, random and block copolymers, and polymers with unique topology.[3] Synthesis and polymerization of ϵ-caprolactone substituted by a functional group is a very efficient way to prepare functional polyesters that are potentially biocompatible and biodegradable for applications in medicine and surgery. There are several literature reports on the synthesis of functional polyesters by ring-opening polymerization of functional monomers.[4] Double bonds in the polyester chains have the advantage of being easily derivatized, e.g., by epoxidation, bromination, and hydrosylilation.[5,6] We have synthesized brominated polyesters by ROP of γ-bromo-ϵ-caprolactone and transferred them into unsaturated polyesters by elimination of HBr.[6] Reaction of γ-bromo-ϵ-caprolactone with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) produces a mixture of three unsaturated ϵ-caprolactones, i.e., 6,7-dihydro-2(5*H*)-oxepinone, 6,7-dihydro-2(3*H*)-oxepinone, and 4,7-dihydro-2(3*H*)-oxepinone (Scheme 2).[6] This mixture is polymerized by $Al(O^{i}Pr)_3$ to produce chains that contain three types of constitutive unsaturated units.

Scheme 1. ADMET Polymerization of Alkyl Ester Diolefin



Scheme 2



This paper reports the synthesis of 6,7-dihydro-2(5*H*)-oxepinone (DHO) and its direct polymerization to produce well-defined aliphatic polyesters. Copolymers with ϵ-caprolactone were also synthesized and their thermal properties studied in relation to the composition of the random copolymers.

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* To whom all correspondence should be addressed.

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Table 1. Molecular Characteristics of Poly(DHO) Initiated by $Al(O^iPr)_3$ in Toluene at Room Temperature

entries	monomer	$[M]_0/[I]_0$	time (min)	conv (%)	$M_{n,th}{}^a \times 10^{-3}$	$M_{n,SEC} \times 10^{-3}$	$M_{n,NMR} \times 10^{-3}$	M_w/M_n
1a	DHO	90	60	71	7.8	11.0		1.15
1b	DHO	90	150	>95	10.5	16.0	9.5	1.15
1c	DHO	37	150	>95	4.3	6.3	4.5	1.20
1d	DHO	170	180	>95	20.0	26.0	18.0	1.15
1e	ϵCL	80	10	100	10.0	10.5^b	9.0	1.15

[a] Theoretical molecular weight for a living polymerization. [b] $M_{n,SEC}$ based on the universal calibration valid to poly(ϵCL).

Experimental Section

Materials. Dichloromethane (Aldrich, 99.9%), light petroleum 40−60 °C (Labotec, 99.9%), phenylselenyl bromide (Aldrich, 98%), diethyl ether (Aldrich, 98%), hydrogen peroxide (Aldrich, 30%), and lithium diisopropylamide (LDA, 2.0 M solution, Aldrich) were used as received. ϵ-Caprolactone (ϵCL) (Janssen Chimica) and hexamethylphosphoramide (HMPA, Aldrich, 99%) were dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use. Toluene (Aldrich, 99.5%) and THF (Aldrich, 99%) were dried by refluxing over calcium hydride and benzophenone−Na, respectively, and distilled under nitrogen atmosphere. Aluminum isopropoxide [$Al(O^iPr)_3$] (Aldrich) was sublimed twice and then dissolved in toluene under nitrogen (0.28 M). 6,7-Dihydro-2(5*H*)-oxepinone (DHO) was synthesized as reported by Fleming et al.[7] and purified by chromatography on silica gel using ether−light petroleum (bp 40−60 °C) (1:1) (R_f 0.2) and dichloromethane (R_f 0.8) as the eluent, respectively. It was further purified by distillation and collected as a colorless liquid (bp 68−69 °C/0.1 mmHg). The final purity of DHO was more than 99% (GC), and it was dried by azeotropic distillation of toluene (three times) just before polymerization.

Polymerization of DHO. In a typical experiment, 1.2 g of DHO (11 mmol) was first added into a previously flamed glass reactor and dried by azeotropic distillation of toluene. Then 10 mL of dry toluene and 0.4 mL of an $Al(O^iPr)_3$ solution (0.28 M in toluene) were added through a rubber septum with a syringe or a stainless steel capillary at room temperature. After 2.5 h, 0.3 mL of 1 N HCl was added, and the reaction mixture was poured into 150 mL of cold heptane. The precipitated polymer was recovered by filtration and dried at 25 °C for 24 h under reduced pressure (96% yield). The molecular weight of poly(DHO) was calculated by ^1H NMR from the relative intensity of the signals of the methyl end group ($\delta = 1.2$ ppm) and the methylene CH_2CO group of the repeat units ($\delta = 4.1$ ppm).

Block polymerization was carried out as follows: 0.4 mL of an $Al(O^iPr)_3$ solution (0.28 M) was added to a solution of ϵ-caprolactone (1.2 g, 10.5 mmol) in toluene (8 mL) at 0 °C. After 45 min, 0.5 mL of the polymerization medium was picked out, and poly(ϵ-caprolactone) [poly(ϵCL)] was precipitated into heptane and analyzed by size exclusion chromatography (SEC) and ^1H NMR. Then a solution of 1.1 g (10 mmol) of dried DHO in 8 mL of toluene was added to the "living" poly(ϵCL)solution at room temperature. After 4 h, 0.3 mL of 1 N HCl was added, and the reaction mixture was poured into 300 mL of cold heptane. The precipitated polymer was separated by filtration and dried at 25 °C for 5 h under reduced pressure (2.2 g, 96% yield). The ϵCL/DHO block copolymer was characterized by SEC, and the composition was analyzed by ^1H NMR from the relative intensity of the signals of the poly(ϵCL) methylene protons ($\delta = 1.4$ ppm) and the poly(DHO) methyl protons ($\delta = 4.7$ ppm). From the copolymer composition and M_n of the first block (SEC and/or ^1H NMR), the molecular weight of the second block was calculated.

Characterization. Size exclusion chromatography (SEC) was performed in THF at a flow rate of 1.0 mL/min at 40 °C using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector. Columns HP PL gel 5μ (10^5, 10^4, 10^3, and 100 Å) were calibrated with polystyrene standards. The universal calibration was used for poly(ϵCL) in reference to the viscometric relationships as reported elsewhere.[8] ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AN 400 apparatus at 25 °C. Differential scanning calorimetry (DSC) was carried out with a Dupont 910 DSC thermal analyzer calibrated with indium. The glass transition temperature and the melting temperature were measured by heating the sample from −100 up to 100 °C at

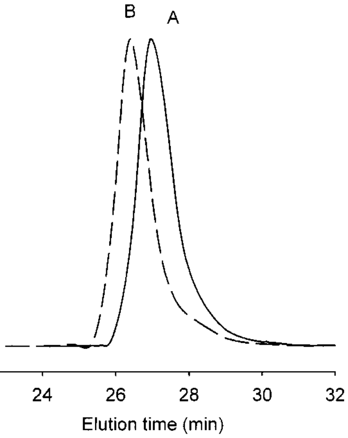

Figure 1. SEC chromatograms for poly(DHO) samples from the same polymerization at two different monomer conversions: (A) 1a in Table 1, conversion 71%, $M_{n,SEC}$ = 11 000; (B) 1b in Table 1, conversion >95%, $M_{n,SEC}$ = 16 000. Conditions: $[M]_0$ = 1.0 M, $[M]_0/[I]_0$ = 90, room temperature.

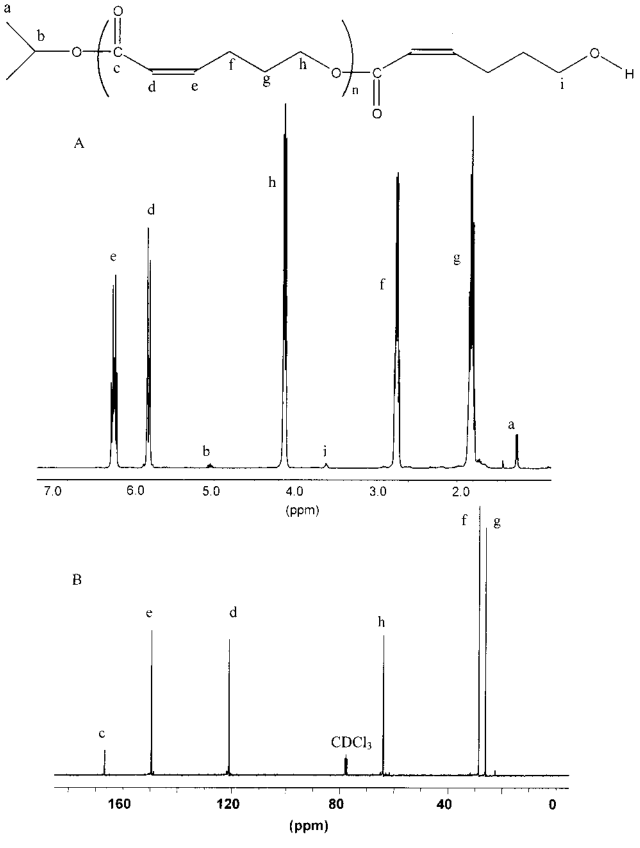

Figure 2. ^1H and ^{13}C NMR spectra of poly(DHO) (1b in Table 1) in $CDCl_3$.

Scheme 3

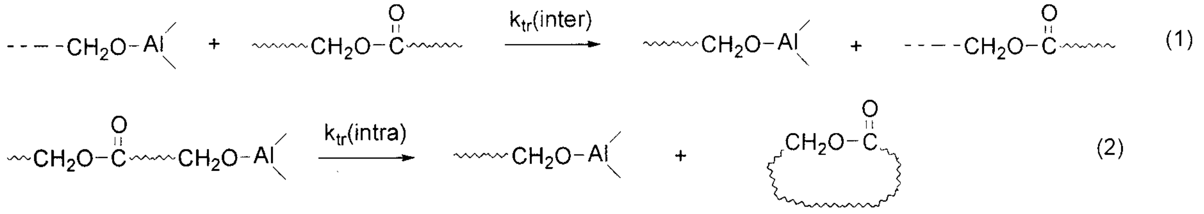

Table 2. Molecular Characteristics of Random Copolymers of ϵCL and DHO Initiated by $Al(O^iPr)_3$ in Toluene at Room Temperature

entries	f^a	time (min)	conv (%)	F^b	$M_{n,th}$ $\times 10^{-3}$	$M_{n,SEC}$ $\times 10^{-3}$	$M_{n,NMR}$ $\times 10^{-3}$	M_w/M_n
2a	0.30	180	>95	0.27	15.3	27.0	14.5	1.20
2b	0.70	180	>95	0.66	15.0	21.0	14.0	1.15
2c	0.42	180	>95	0.40	15.0	21.0	14.0	1.25

[a] Molar fraction of DHO in the comonomer feed. [b] Molar fraction of poly(DHO) in the random copolymer (determined by ^{1}H NMR analysis).

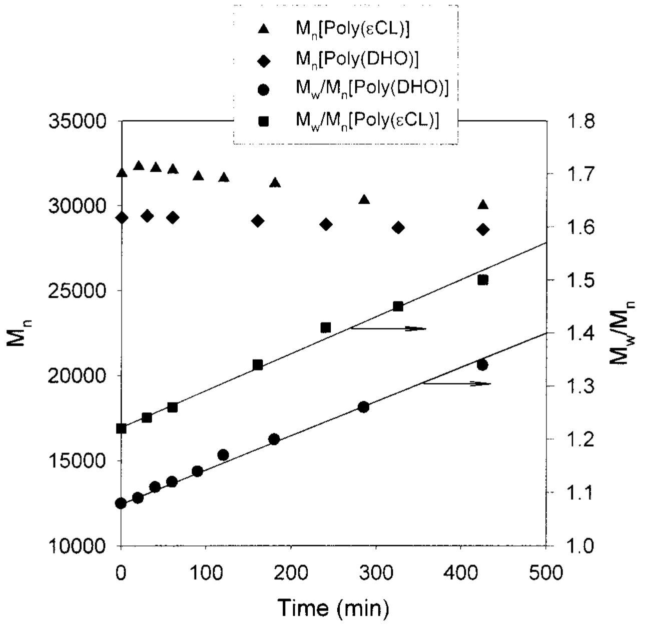

Figure 3. Time dependence of M_n and M_w/M_n for living poly(ϵCL) and poly(DHO) after complete monomer conversion, in toluene at room temperature. $[Al(O^iPr)_3]_0 = 7.8 \times 10^{-3}$ M, $[M]_0 = 1.0$ M.

10 °C/min. Thermogravimetric analysis was carried out with a DuPont 51 thermogravimetric analyzer over the 25−550 °C temperature range at a 10 °C/min rate under a nitrogen flow.

Results and Discussion

6,7-Dihydro-2(5*H*)-oxepinone (DHO) is an unsaturated ϵ-caprolactone with the C═C conjugated with the carbonyl. It was synthesized according to the literature[6] and carefully purified by chromatography on silica gel and distillation under reduced pressure.

The DHO polymerization was initiated by aluminum isopropoxide [$Al(O^iPr)_3$] at different monomer to $Al(O^iPr)_3$ molar ratios in toluene at room temperature. Table 1 shows that the polymerization is slower than that of ϵ-caprolactone (entries 1a and 1e). The reactivity of DHO is most likely reduced by conjugation of the carbonyl group with the internal double bond. The experimental (^{1}H NMR) and theoretical molecular weights ($M_{n,th}$), based on the monomer-to-initiator molar ratio and the monomer conversion, agree well with a well-controlled polymerization process. Figure 1 compares the SEC chromatograms for poly(DHO) at 71% and semiquantitative conversion, respectively (samples 1a and 1b, in Table 1). The polydispersity remains low (1.15−1.20), which indicates that initiation is fast relative to propagation, and propagation is fast compared to any chain transfer or termination reactions. Figure 2A shows the ^{1}H NMR spectrum of a typical poly(DHO) homopolymer (sample 1b in Table 1, $M_{n,NMR} = 9500$, $M_w/M_n = 1.15$). The major peaks of this spectrum can be assigned to the protons of the polyester backbone, the isopropyl ester end group ($\delta = 5.0$ and 1.2 ppm), and the methylene conjoint to the hydroxyl end group ($\delta = 3.8$ ppm). The coupling constants for the unsaturated protons of poly(DHO) (12.5 Hz) and DHO (11.8 Hz) indicate that the configuration of the double bonds are the same before and after polymerization. Both the monomer and polymer have a cis configuration. These data are consistent with a coordination−insertion polymerization mechanism that implies selective cleavage of the acyl−oxygen bond of the cyclic monomer. There is no evidence for transesterification side reaction. The ^{13}C NMR spectrum of the polymer and the peak assignment are shown in Figure 2B, which also confirms the structure expected for the polymer.

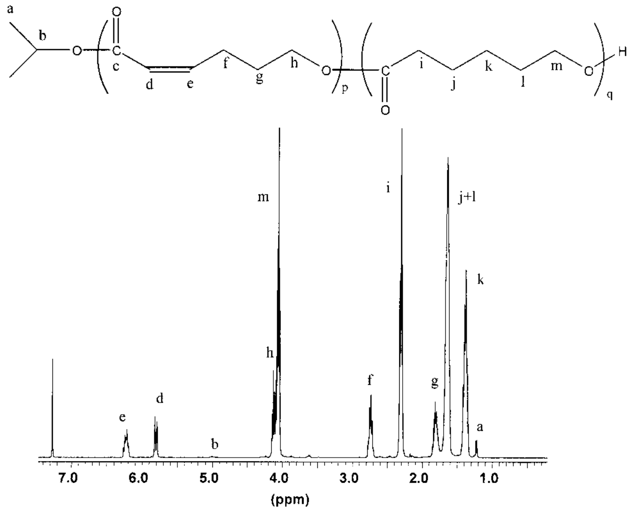

Figure 4. ^{1}H NMR spectrum of poly(CL-*co*-DHO) (2a in Table 2) in $CDCl_3$.

All of these data show that the polymerization of DHO initiated by $Al(O^iPr)_3$ at room temperature is living, as is the case for the ϵCL polymerization at 0 °C, all the other conditions being the same. It is however known that M_n and M_w/M_n of the poly(ϵCL) chains do not remain constant beyond the time required for the monomer conversion to be complete.[3a] Indeed, transesterification reactions take place (Scheme 3), which broadens the molecular weight distribution (intermo-

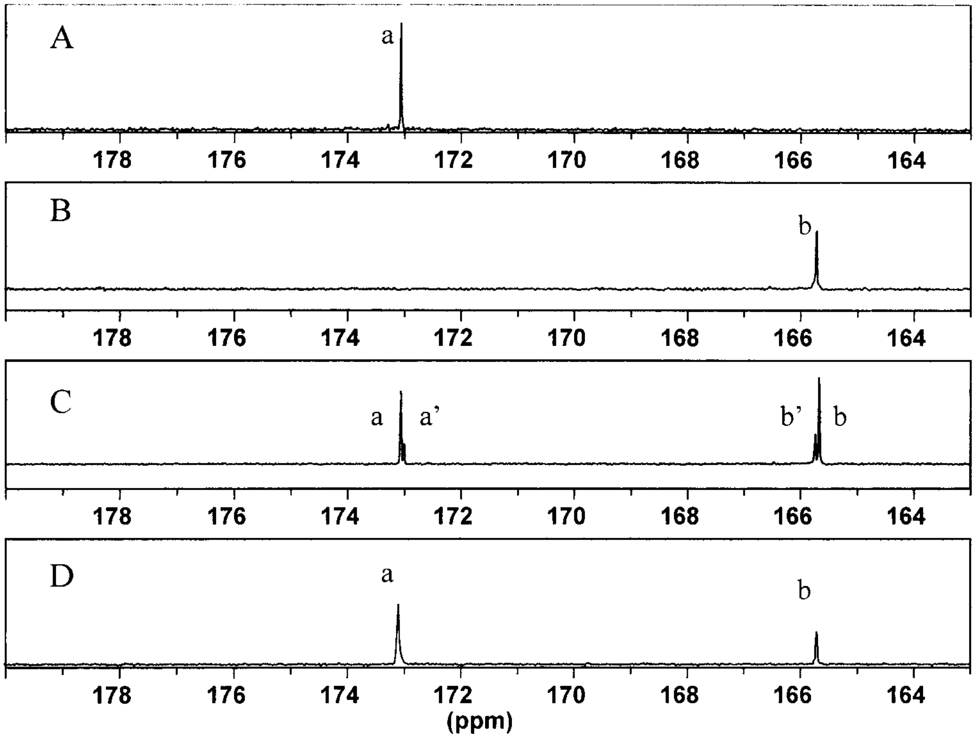

Figure 5. Expanded ^{13}C NMR spectra (carbonyl region) of (A) poly(ϵCL) (1e in Table 1), (B) poly(DHO) (1b in Table 1), (C) poly(CL-*co*-DHO) (2b in Table 2), and (D) poly(CL-*b*-DHO) (3a in Table 3).

lecular reactions, eq 1) and decreases M_n (intramolecular reactions, eq 2). The occurrences of transesterification in the polymerization of ϵCL and DHO are compared by reporting the time dependence of M_n and M_w/M_n for living poly(ϵCL) (M_n = 32 000, M_w/M_n = 1.08) and poly(DHO) (M_n = 29 000, M_w/M_n = 1.22) chains (complete monomer conversion) at room temperature. Only a slight decrease in M_n is observed for the two polymers over 425 min, which is consistent with very slow intramolecular transesterification. In contrast, M_w/M_n increases, although at the same rate for poly(ϵCL) and poly(DHO). Because the DHO polymerization is slower than that one of ϵCL, the selectivity parameter, β, which is defined as the ratio of the propagation rate constant to the transfer rate constant, is slower for DHO than for ϵCL.

A mixture of DHO with ϵ-caprolactone was also polymerized by aluminum isopropoxide [Al(O^{i}Pr)$_3$] in toluene at room temperature (Table 2). The experimental molecular weight agrees with the value calculated from the monomer-to-initiator molar ratio, and the molecular weight distribution is narrow. The ^{1}H NMR spectrum shown in Figure 4 is consistent with the excepted structure. These data agree with a controlled random copolymerization. Figure 5 compares the carbonyl region of the ^{13}C NMR spectra of both homopolymers (Figure 5A,B) and copolymer 2b in Table 2 (Figure 5C). Peaks a and b are assigned with the homodiads of poly(ϵCL) and poly(DHO), respectively. The two additional a′ and b′ peaks observed in the carbonyl region for the copolyester are thus characteristic of the ϵCL/DHO heterodiads and confirm the randomness of the structure. The low intensity of peaks a′ and b′ compared to that of peaks a and b is a consequence of the faster polymerization of ϵCL than DHO. Because ϵCL is consumed more rapidly than DHO, ϵCL homodiads dominate at the beginning of the copolymerization, whereas more DHO homodiads are formed at the end of the controlled polyaddition. Therefore, the copolymer structure is not ideally statistic but close to a gradient distribution of the comonomers.

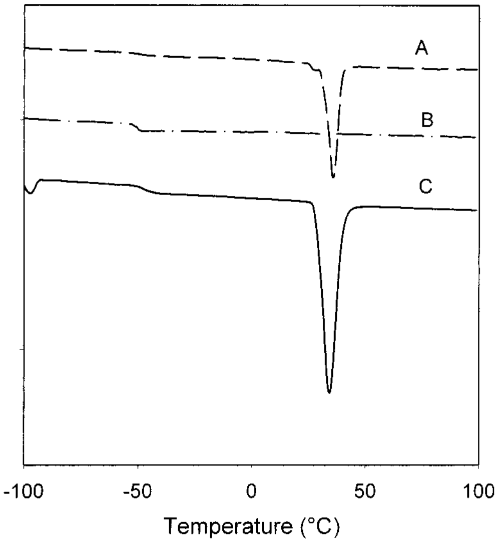

Figure 6. DSC traces for poly(DHO) (1d in Table 1) at a scan rate of 10 °C/min: (A) first scan, (B) second scan (2 h later than first scan), (C) third scan (24 h later than first scan).

The thermal properties of the (co)polymers were analyzed by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. Figure 6 shows the DSC traces of poly(DHO) with different thermal histories. The first scan shows that poly(DHO) is semicrystalline with a T_g at −50 °C and T_m at 35 °C. The second scan is recorded after the sample being kept at room temperature for 2 h; no melting temperature is observed. The third scan after 24 h shows again a melting endotherm, which is consistent with a slow crystallization. Copolymerization of ϵCL with increasing amounts

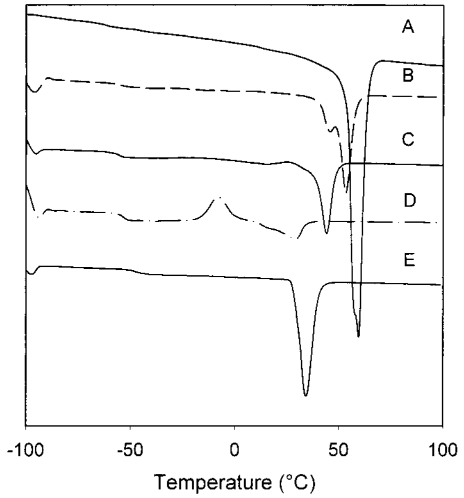

Figure 7. DSC traces at 10 °C/min of poly(CL-*co*-DHO) copolyesters with various molar compositions: (A) $F_{DHO} = 0$ (1d in Table 1), (B) $F_{DHO} = 0.27$, (C) $F_{DHO} = 0.40$, (D) $F_{DHO} = 0.66$, (E) $F_{DHO} = 1$ (1d in Table 1).

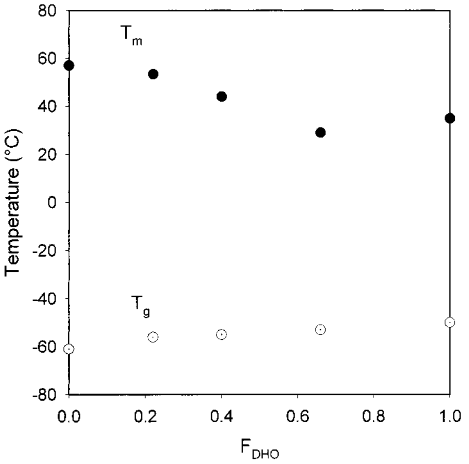

Figure 8. Phase diagram for poly(CL-*co*-DHO) copolyesters.

of DHO has a strong effect on the melting temperature (T_m) (Figure 7). Poly(ϵCL) shows a T_g at −61 °C and a T_m at 57 °C. As the DHO content increases, T_m decreases from 57 to 29 °C at $F_{DHO} = 0.66$, followed by an increase up to T_m of the homopoly(DHO) (35 °C) (Figure 8). The T_g dependence on the copolymer composition apparently agrees with the Fox−Flory relationship[9] (Figure 8). Thermogravimetric analysis (TGA) of homopolymer and random copolymer is illustrated in Figure 9. Poly(DHO) is more thermally stable than poly(ϵCL). The TGA trace for the random copolymer is intermediate between the thermograms for poly(DHO) and poly(ϵCL). The residue observed at high temperature (10% for poly(DHO) and 5% for random copolymer) might be due to reaction of the C=C at high temperature (cross-linking).

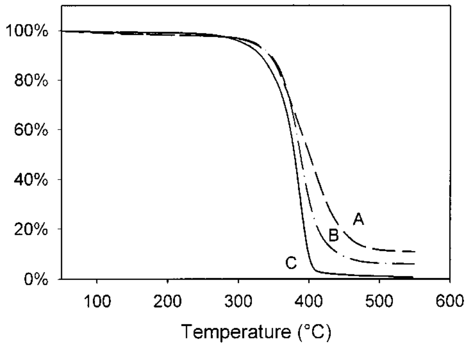

Figure 9. Thermogravimetric analysis of poly(DHO) (1d in Table 1) (A), poly(CL-*co*-DHO) (3b in Table 3) (B), and poly(ϵCL) (1e in Table 1) (C) under nitrogen, at 10 °C/min.

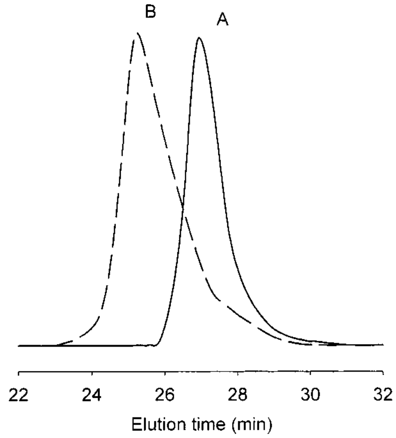

Figure 10. SEC chromatograms of a diblock copolymer and its poly(ϵCL) precursor: (A) first poly(ϵCL) block, $M_n = 10\,000$; (B) poly(CL-*b*-DHO) (3b in Table 3), $M_n = 10\,000/10\,000$.

Finally, block copolymers of ϵCL and DHO were prepared by sequential polymerization of the two monomers, ϵCL being added first in one experiment and after DHO in a second experiment. The molecular weight calculated for each block is consistent with the value expected for a living polymerization at complete monomer conversion (Table 3). Furthermore, the molecular weight distribution of the copolymer remains narrow ($M_w/M_n < 1.25$). Figure 10 compares the SEC chromatograms of the first poly(ϵCL) block and the poly(CL-*b*-DHO) diblock copolymer. The chromatogram of the macroinitiator systematically shifts toward higher molecular weight with no clear evidence that part of the poly(ϵCL) chains have not initiated the DHO polymerization. The slight increase in the polydispersity upon copolymerization might result from slower initiation of DHO by the poly(ϵCL) macroinitiation compare to propagation. We have not identified a solvent selective for either poly(ϵCL) or poly(DHO). ^{13}C NMR confirms that the copolymerization product is pure diblock, i.e., that no transesterification has occurred between the poly(ϵCL) and the poly(DHO) blocks. This transesteri-

Table 3. Sequential Polymerization of ϵCL and DHO Initiated by Al(O^{i}Pr)$_3$ in Toluene

	first block							second block							
entries	monomer	$[M]_0/[I]_0$	temp (°C)	conv (%)	$M_{n,th}$ $\times 10^{-3}$	$M_{n,SEC}$ $\times 10^{-3}$	M_w/M_n	monomer	$[M]_0/[I]_0$	temp (°C)	conv (%)	$M_{n,th}$ $\times 10^{-3}$	$M_{n,NMR}$ $\times 10^{-3}$	$M_{n,SEC}$ $\times 10^{-3}$	M_w/M_n
3a	ϵCL	88	0	99	10.0	11.0[a]	1.15	DHO	45	25	>95	5.0	4.7	17.0	1.20
3b	ϵCL	88	0	99	10.0	10.5[a]	1.15	DHO	89	25	>95	10.0	8.0	25.0	1.25
3c	DHO	90	25	99	10.0	15.6	1.20	ϵCL	88	0	>95	10.0	9.5	29.0	1.25

[a] $M_{n,SEC}$ based on the universal calibration valid to poly(ϵCL).

fication reaction would result in mixed sequences easily detected by additional a′ and b′ resonances, as was observed in the carbonyl region for the random copolymer (Figure 5C). Figure 5D shows only the two homodiad peaks characteristic of each homopolymer and no trace of heterodiad peaks. Furthermore, the relative intensity of the homodiad peaks confirms the asymmetric comonomer composition of the copolymer, in agreement with the ^{1}H NMR analysis.

Conclusions

Homopolymerization of the 6,7-dihydro-2(5*H*)-oxepinone initiated by $Al(O^iPr)_3$ in toluene at room temperature leads to unsaturated aliphatic polyesters of predictable molecular weight and narrow molecular weight distribution. NMR observation of the α-isopropyl and ω-hydroxy end groups is consistent with a coordination−insertion mechanism. Beyond the complete monomer conversion, mainly intermolecular transesterification occurs in the case of poly(DHO) and poly(ϵCL) at the same rate at 25 °C. The poly(DHO) homopolymer is semicrystalline with a glass transition temperature at −50 °C and a melting temperature at 35 °C. Controlled random copolymerization of ϵCL and DHO is successful in toluene at room temperature. Similarly, block copolymers are easily prepared in a controlled way, by first polymerizing ϵCL or DHO in toluene. Increasing the DHO content of the random copolymer decreases T_m and increases T_g compared to the case of poly(ϵCL). Copolymerization is thus an easy way to modulate the characteristics of unsaturated aliphatic polyesters. The unsaturated polyesters backbone offers sites for cross-linking, which is useful for the synthesis of biodegradable and biocompatible (hydro)gels. Moreover, the double bond can be easily derivatized into a series of functional groups, thereby leading to new properties of functional aliphatic polyesters.

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