e-Polymers **2002**, no. 034. http://www.e-polymers.org

Novel unsaturated ε-caprolactone polymerizable by ring-opening and ring-opening metathesis mechanisms

Xudong Lou, *Christophe Detrembleur* [1], *Philippe Lecomte*, *Robert Jérôme**

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6a, 4000 Liège, Belgium; Fax (32)4-3663497; rjerome@ulg.ac.be

[1] Present address: Bayer AG, Leverkusen, Germany

(Received: June 12, 2002; published: August 8, 2002)

Abstract: Ring-opening polymerization (ROP) and ring-opening metathesis polymerization (ROMP) of an unsaturated ε-caprolactone, 6,7-dihydro-2(3*H*)-oxepinone (DHO2), are alternative routes to produce unsaturated aliphatic polyesters with the same molecular structure. Polymerization of DHO2 initiated by Al isopropoxide in toluene at room temperature or at 0°C proceeds by a coordination-insertion mechanism, although intramolecular transesterification takes place beyond complete monomer conversion. The molecular weight distribution is narrow as long as monomer conversion does not exceed 90%. Ring-opening metathesis polymerization of DHO2 initiated by Schrock's Mo-based catalyst, **1**, at 60°C allows higher molecular weight unsaturated polyester to be prepared, even though an intramolecular side reaction also operates. The structure of poly(DHO2) synthesized by ROP and ROMP is the same, as confirmed by ^{1}H, ^{13}C NMR, and FT-IR spectra. Copolymers of DHO2 with norbornene, *cis*-cyclooctene, and 1,5-cyclooctadiene have been successfully prepared.

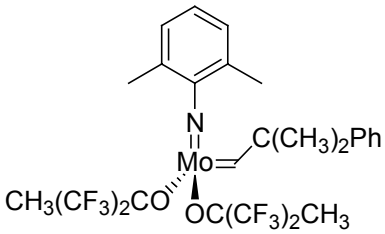
Introduction

Nowadays, steadily increasing attention is paid to biodegradable polymers not only for potential applications in agricultural and medical fields but also for the waste management of plastics [1]. Ring-opening polymerization (ROP) of lactones, lactides, and glycolide is commonly used to synthesize biodegradable aliphatic polyesters. However, it is quite a problem to chemically attach active molecules (drug, recognition agent, adhesion promoter, probe) onto these polyesters, which is a limitation for a series of applications. In the recent past, ε-caprolactone has been chemically modified [2-8], and functionalized aliphatic polyesters have accordingly been made available. Among other achievements, unsaturated ε-caprolactone has been synthesized and polymerized into unsaturated aliphatic polyesters in a controlled manner [6-8]. Double bonds in the polyester chains have the advantage of being easily derivatized, e.g., by crosslinking reaction, epoxidation, bromination, and hydrosylilation. Parallel to progress in ROP of cyclic (di)esters, substantial advances have been reported in ring-opening metathesis polymerization (ROMP) of cyclic olefins, as result of the discovery of efficient catalysts, such as Schrock's catalysts (**1** in Scheme 1, and the analogous tungsten system), and Grubbs' catalysts (**2** in Scheme 1) [9].

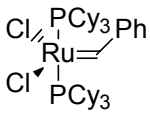
Combination of two polymerization mechanisms is known to be rewarding in block and graft copolymerization. As an example of combination of ROP and ROMP, some of us have reported that living ROP of ε-caprolactone is an easy way to prepare

norbornene end-capped poly(ε-caprolactone) macromonomers that can be copolymerized by ROMP with norbornene and formation of poly(norbornene)-*graft*-poly(ε-caprolactone) copolymer [10]. In an alternative strategy, dual monomers can be polymerized by two different mechanisms and lead to polymers with a completely different structure. For instance, γ-acryloyloxy-ε-caprolactone can be polymerized in a controlled/living manner by atom transfer radical polymerization (ATRP) and ROP [6]. Polyacrylates bearing pendent ε-caprolactone units are formed by ATRP, whereas ROP leads to polyesters with pendent acrylate groups, which makes them crosslinkable [11] and electrograftable onto metallic surfaces [12]. At our best knowledge, there is no report that a dual monomer is polymerizable by ROP and ROMP.

Scheme 1



1



2

This paper reports on the (co)polymerization of 6,7-dihydro-2(3*H*)-oxepinone (DHO2) by two different processes, coordinative ROP and ROMP. Homopolymerization of DHO2 initiated by aluminium isopropoxide [Al(O^iPr)$_3$] in toluene has been studied at different temperatures. Metathesis polymerization of DHO2 initiated by Schrock's catalyst **1** has been carried out, and the molecular structure of the formed polymers has been compared by different techniques. Copolymerization of DHO2 with norbornene, *cis*-cyclooctene, and 1,5-cyclooctadiene is also part of this study.

Experimental part

Materials

Schrock's catalyst (**1**), and Grubbs' catalyst (**2**) were purchased from Strem and used as received. ε-Caprolactone (εCL) (Aldrich, 99%), *cis*-cyclooctene (Aldrich, 95%), and 1,5-cyclooctadiene (Aldrich, 99%) were dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use. Norbornene (Aldrich, 99%) was sublimated and stored under nitrogen. Toluene and tetrahydrofuran (THF) (Aldrich) were dried by refluxing over calcium hydride and benzophenone-Na mixture, respectively, and distilled under nitrogen atmosphere. 6,7-Dihydro-2(3*H*)-oxepinone (DHO2) was prepared as reported elsewhere [13]. Aluminium isopropoxide [Al(O^iPr)$_3$] (Aldrich) was sublimated twice and then dissolved in toluene under nitrogen (0.06 M).

Polymerization of DHO2 initiated by Al(O^iPr)$_3$

In a typical experiment, 0.5 g of DHO2 (4.5 mmol) was first added into a previously flamed glass reactor and dried by azeotropic distillation of toluene (three times). Then 4 mL of dry toluene and 0.4 mL of an Al(O^iPr)$_3$ solution (0.06 M in toluene) were added through a rubber septum with a syringe or a stainless steel capillary at 0°C.

After 45 min, 0.2 mL of 1 M HCl was added, the reaction mixture was analyzed by ^{1}H NMR spectroscopy (80% monomer conversion) and then 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. The degree of polymerization (DP) of poly(DHO2) was calculated from the relative intensity of the ^{1}H NMR signals at 1.2 and 4.1 ppm, viz., DP = 147 and $M_{n,NMR}$ = 16 500.

Metathesis polymerization of DHO2

In a typical experiment, 0.8 g (7.1 mmol) of DHO2 was added into a 25 mL glass reactor and degassed by repeated nitrogen-vacuum cycles (three times). 12 mg (0.016 mmol) of Schrock's catalyst **1** was added into the reactor (in a dry-box), that was heated at 60°C for 24 h. After addition of 8 mL of toluene, the polymer was precipitated in 100 mL of heptane, filtrated and dried at 25°C for 24 h under reduced pressure (yield 61%).

Metathesis copolymerization of DHO2

The procedure was the same as for homopolymerization. The comonomers were norbornene in toluene (1.5 M), *cis*-cyclooctene, and 1,5-cyclooctadiene.

DHO2/norbornene copolymer, ^{1}H NMR ($CDCl_3$): δ = 5.7 (m, 1H, -C*H*=CH-), 5.55 (m, 1H, -C*H*=CH-), 5.35 (s, 6.08H, -C*H*=CH-), 5.20 (m, 23.7H, -C*H*=CH-), 4.1 (t, 2H, -CH_2-OCO-), 3.1 (d, 2H, -CH_2-CO-), 2.8 (s, 23.2H, -C*H*-), 2.4 (m, 8.2H, -CH_2-CO-, -C*H*-), 2.3 (m, 2H, -CH_2-CH_2-OCO-), 2.0 - 1.7 (m, 46H, -CH_2CH_2-), 1.3 (m, 31H, -CH_2CH_2-) and 1.0 ppm (m, 15H, -CH_2-). The molar content of DHO2 (F_{DHO2}) in the copolymer was calculated from the relative intensity of the signals at 5.5 - 5.7 and 5.1 - 5.4 ppm, viz., F_{DHO2} = 0.06.

DHO2/*cis*-cyclooctene copolymer, ^{1}H NMR ($CDCl_3$): δ = 5.7 (m, 1H, -C*H*=CH-), 5.55 (m, 1H, -C*H*=CH-), 5.4 (m, 12H, -C*H*=CH-), 4.1 (t, 2H, -CH_2-OCO-), 3.1 (d, 2H, -CH_2-CO-), 2.3 (m, 2H, -CH_2-CH_2-OCO-) and 1.9 ppm (m, 24H, -CH_2-). F_{DHO2} was calculated from the relative intensity of the signals at 5.5 - 5.7 and 5.4 ppm, viz., F_{DHO2} = 0.14.

DHO2/1,5-cyclooctadiene copolymer, ^{1}H NMR ($CDCl_3$): δ = 5.7 (m, 1H, -C*H*=CH-), 5.55 (m, 1H, -C*H*=CH-), 5.4 (m, 21.2H, -C*H*=CH-), 4.1 (t, 2H, -CH_2-OCO-), 3.1 (d, 2H, -CH_2-CO-), 2.3 (m, 2H, -CH_2-CH_2-OCO-), 2.1 ppm (m, 44.5H, -CH_2-). F_{DHO2} was calculated from the relative intensity of the signals at 5.5 - 5.7 and 5.4 ppm, viz., F_{DHO2} = 0.09.

Degradation of DHO2/1,5-cyclooctadiene copolymer

0.5 mL of conc. HCl (37%) was added to a solution of 0.4 g of copolymer (3d in Tab. 3) in 10 mL of 1,4-dioxolane and stirred at 80°C overnight. Then, the polymer was recovered by precipitation in 150 mL of methanol, filtered and dried at 25°C overnight (yield 0.25 g). ^{1}H NMR ($CDCl_3$): δ = 5.4 (2H, -C*H*=C*H*-), 2.1 ppm (4H, -CH_2-).

Characterization

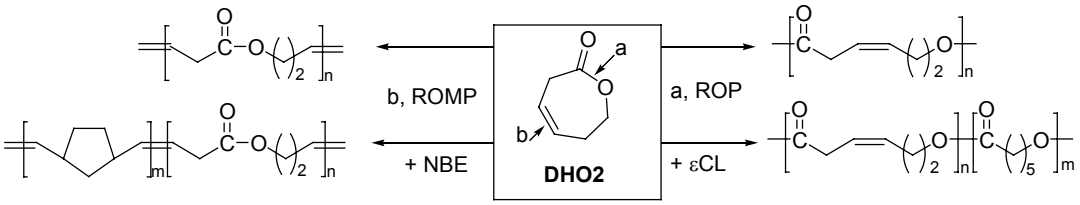
Size exclusion chromatography (SEC) was performed in THF at a flow rate of 1.0 mL/min at 40°C using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector. Columns HP PL gel 5µ (10^5 Å, 10^4 Å, 10^3 Å, 100 Å) were calibrated with polystyrene standards. ^{1}H NMR and ^{13}C

NMR spectra were recorded in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AM 400 apparatus at 25°C.

Results and discussion

6,7-Dihydro-2(3*H*)-oxepinone (DHO2) is an unsaturated ε-caprolactone with an inner C=C in β-position with respect to the carbonyl (Scheme 2). It is a dual monomer, because the cyclic ester is polymerizable by ROP and the cyclic olefin is polymerizable by ROMP. Recently, ring-opening copolymerization of DHO2 with ε-caprolactone was initiated by $Al(O^iPr)_3$, and unsaturated aliphatic polyesters were prepared in a living manner as assessed by the agreement between experimental molecular weight at total monomer conversion and M_n predicted from the initial monomer-to-initiator mole ratio[13]. Polydispersity was reasonably low ($M_w/M_n \leq 1.2$).

Scheme 2



Tab. 1. Molecular characteristics of poly(DHO2) initiated by $Al(O^iPr)_3$ in toluene at different temperatures

Entries	$[M]_0/[I]_0$	Temp. in °C	Time in min	Conv. [a] in %	$M_{n,th}$ [b] $\times10^{-3}$	$M_{n,SEC}$ [c] $\times10^{-3}$	$M_{n,NMR}$ $\times10^{-3}$	M_w/M_n
1a	54	25	55	99	6.0	6.6	-	2.25
1b	54	25	20	90	5.4	8.2	5.3	1.20
1c	190	25	28	78	16.6	20.5	16.0	1.30
1d	190	0	45	80	17.0	27.0	16.5	1.15
1e	40	0	25	85	3.8	5.4	3.6	1.20
1f	190	0	120	100	21.0	18.2	-	1.50

[a] Conversion calculated from ^1H NMR spectroscopy. [b] Theoretical molecular weight for a living polymerization. [c] $M_{n,SEC}$ based on polystyrene calibration.

Homopolymerization of DHO2 has been initiated by $Al(O^iPr)_3$ at different monomer-to-initiator mole ratios in toluene at 25°C and 0°C. Tab. 1 shows that the molecular weight distribution of the polymer prepared at room temperature and complete monomer conversion is broad (M_w/M_n = 2.25, entry 1a), which is evidence for the occurrence of an intramolecular transesterification reaction [13]. Only when the polymerization is stopped by HCl before monomer conversion exceeds 90%, poly(DHO2) of low M_w/M_n is collected (entries 1b and 1c). In order to decrease the extent of transesterification reactions, the reaction temperature has been decreased

to 0°C, and lower M_w/M_n has been accordingly observed (entries 1d and 1e). Fig. 1 shows the proton NMR spectrum of a typical homopolymer (1e in Tab. 1, $M_{n,NMR}$ = 3 600, M_w/M_n = 1.20). The major peaks of this spectrum can be assigned to the protons of the polyester backbone. The observation of an isopropyl ester end-group (δ = 5.0 and 1.2 ppm) together with the methylene adjacent to the hydroxyl end-group (δ = 3.65 ppm) indicates that homopolymerization proceeds by a coordination-insertion mechanism. Even at 0°C, side reactions take place at very high monomer conversion (entry 1f, in Tab. 1), which is confirmed by ^{13}C NMR.

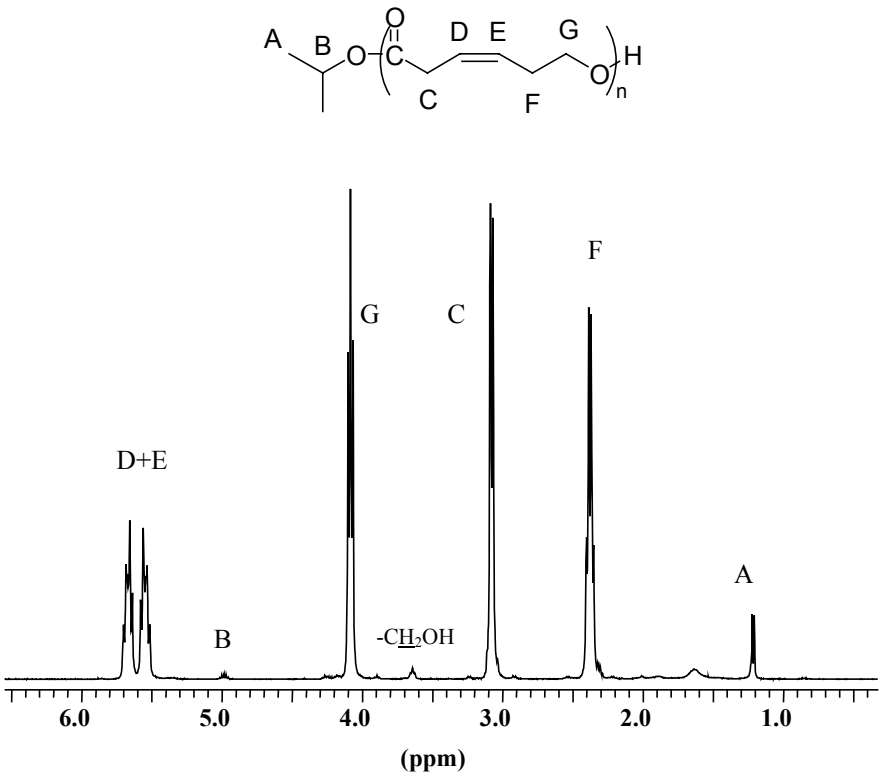


Fig. 1. ^{1}H NMR spectrum of poly(DHO2) initiated by Al(O^{i}Pr)$_3$ in toluene at 0°C. Solvent: $CDCl_3$

Fig. 2 compares the ^{13}C NMR spectra for the monomer DHO2 (Fig. 2A), for polymer 1d (Tab. 1; M_w/M_n = 1.15) (Fig. 2B) and for polymer 1c (Tab. 1; M_w/M_n = 1.30) (Fig. 2C). The major resonances fit the structure expected for poly(DHO2). Furthermore, the signals at 129.0 and 124.8 ppm for the C=C double bond indicate the same *cis* configuration before and after polymerization. Additional resonances of low intensity (128.5, 125.2, 65.2, 58.0, 35.3, 28.8, and 23.4 ppm, a' - g') are observed for the two poly(DHO2) samples. Because intramolecular transesterification is known to take place in homopolymerization of DHO2, these additional signals can be reasonably assigned to cyclics formed by this process. From the integration of the peaks, *c*. 1% of cyclics contaminate the lower-polydispersity sample (M_w/M_n = 1.15) compared to *c*. 2% for the second sample (M_w/M_n = 1.30). It is known that the growth of polylactide chains initiated by Al(O^{i}Pr)$_3$ is limited by competing transesterification reactions[15]. These side reactions also occur, even at low temperature, in case of the homopolymerization of DHO2. Furthermore, when the theoretical molecular weight is high, a very small amount of initiator is required, which makes the polymerization much more sensitive to impurities.

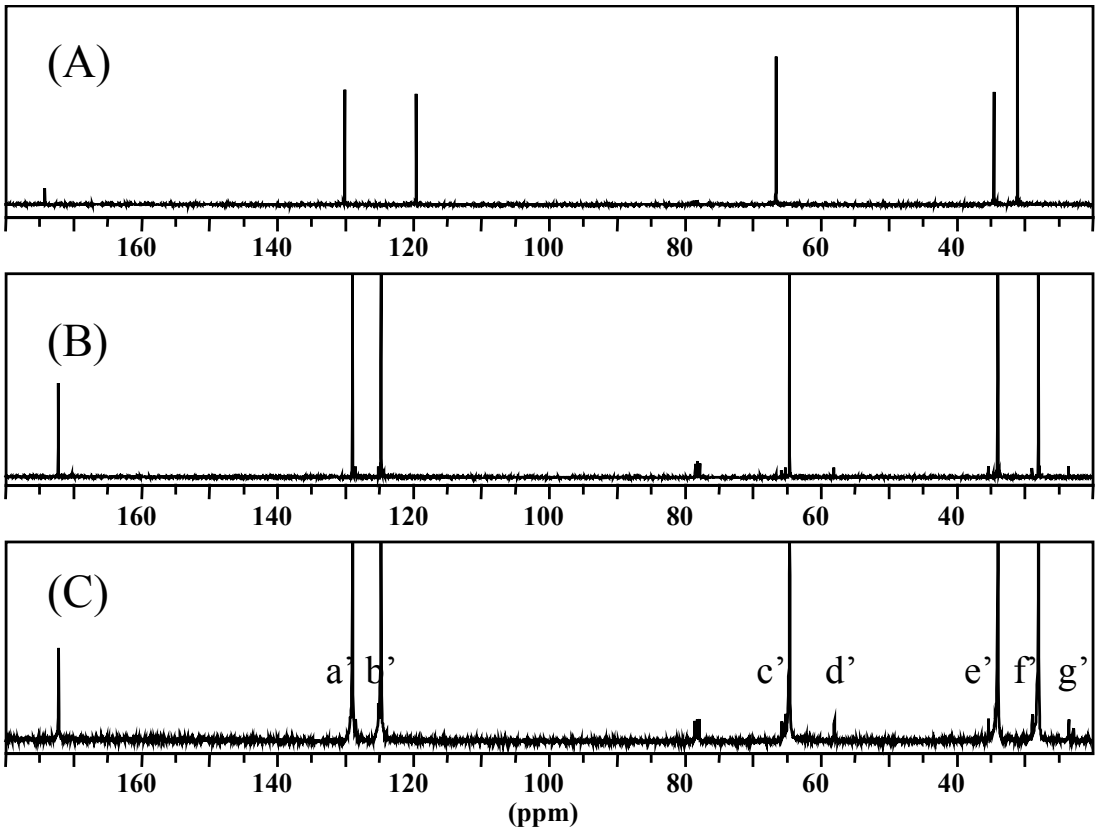


Fig. 2. ^{13}C NMR spectra of (A) monomer DHO2; (B) poly(DHO2) (1d in Tab. 1; M_w/M_n = 1.15); (C) poly(DHO2) (1c in Tab. 1; M_w/M_n = 1.30). Signals a' - g' refer to cyclics

Because the double bond of DHO2 is part of the cyclic structure, polyester with the same molecular structure is expected to be formed by ROP and ROMP (Scheme 2). Compared to $Al(O^iPr)_3$, the metathesis catalysts (**1** and **2** in Scheme 1) are not very sensitive to impurities.

Tab. 2. Ring-opening metathesis polymerization of DHO2 initiated by **1** and **2** in bulk at 25 and 60°C

Entry	Catalyst (%)	Time in h	Temp. in °C	Yield in %	$M_{n,SEC}$ [a] $\times 10^{-4}$	M_w/M_n
2a	**1** (3.0)	24	25	0	-	-
2b	**1** (3.0)	3	60	30	1.9	1.80
2c	**1** (2.0)	24	60	72	5.4	2.15
2d	**1** (1.5)	4.5	60	50	5.0	1.95
2e	**1** (1.5)	24	60	61	6.2	2.10
2f	**2** (3.0)	24	60	0	-	-

[a] $M_{n,SEC}$ based on calibration with polystyrene standards.

Metathesis polymerization of DHO2 has been initiated by the Mo-based Schrock catalyst **1** and Grubbs' catalyst **2** in bulk at 25 and 60°C. Tab. 2 shows that no polymer is formed at 25°C in the presence of **1**. When the temperature is increased up to 60°C, the monomer conversion is 30% after 3 h. Lower catalyst content results in lower polymerization yield and higher M_n, all the other conditions being the same (entries 2c and 2e, Tab. 2). Expectedly under quite comparable conditions, monomer conversion and M_n increase with reaction time (entries 2d and 2e). The molecular weight distribution is however broad ($M_w/M_n \geq 1.8$), which may indicate the occurrence of parasitic reactions (as will be discussed later). Long poly(DHO2) chains ($M_{n,SEC}$ > 50 000) can be now prepared, which is difficult by ROP. No polymerization is observed with Grubbs' catalyst **2** at 60°C for 24 h. ^{1}H NMR spectroscopy (entry 2e in Tab. 2) with the same major peaks as in Fig. 1 confirms the structure expected for poly(DHO2) (Fig. 3).

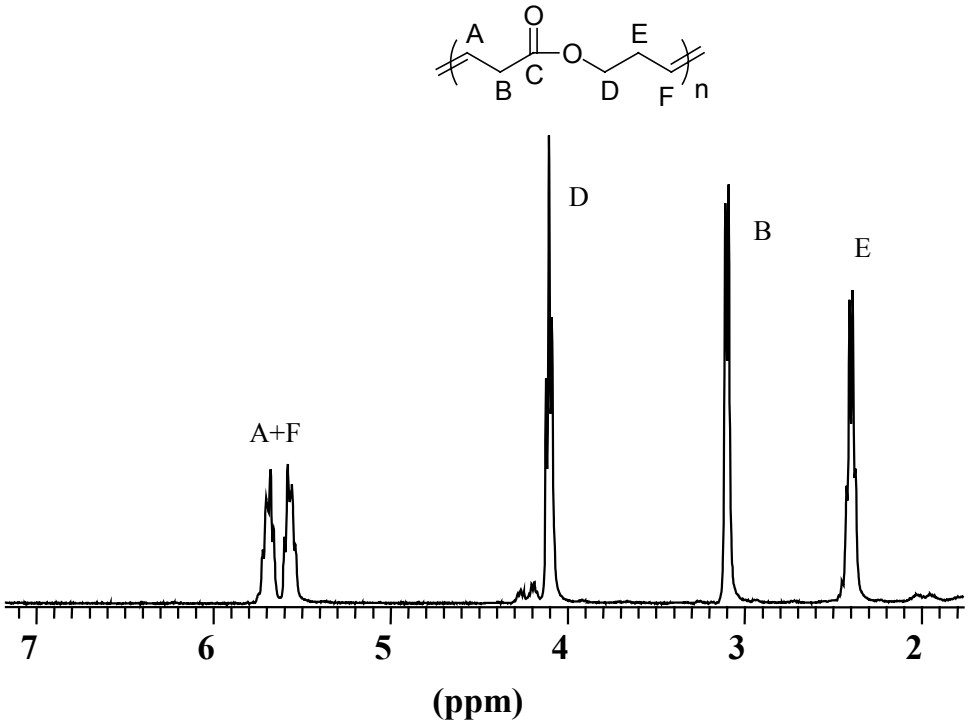


Fig. 3. ^{1}H NMR spectrum of poly(DHO2) initiated by **1** in bulk at 60°C (2c in Tab. 2). Solvent: $CDCl_3$

The ^{13}C NMR spectrum (Fig. 4) is also in agreement with the one recorded for the ROP product (Fig. 2C). Thus, the C=C bonds have *cis*-configuration, although metathesis polymerization of cycloheptene and cyclooctene usually leads to polymers with a mixed *cis*/*trans* configuration [16]. The observation of the same additional resonances of low intensity (a' - g') as for the ROP product must be noted. According to Grubbs et al., backbiting reactions in ROMP of low strained cycloolefins are responsible for a broader molecular weight distribution [17]. This is an extra, although indirect, evidence of the assignment of the low-intensity signals to cyclics. Although poly(DHO2) with molecular weight ($M_{n,SEC}$) as high as 62 000 can be prepared, this side reaction prevents very long chains from being produced. FT-IR spectra of poly(DHO2) prepared by ROP and ROMP are shown in Fig. 5. These spectra are also identical, and the absorptions at 1658 and 707 cm^{-1} confirm the

double bond configuration. Whatever the polymerization mechanism, ROP or ROMP, the same polymer is formed, which is the expected unsaturated poly(ε-caprolactone).

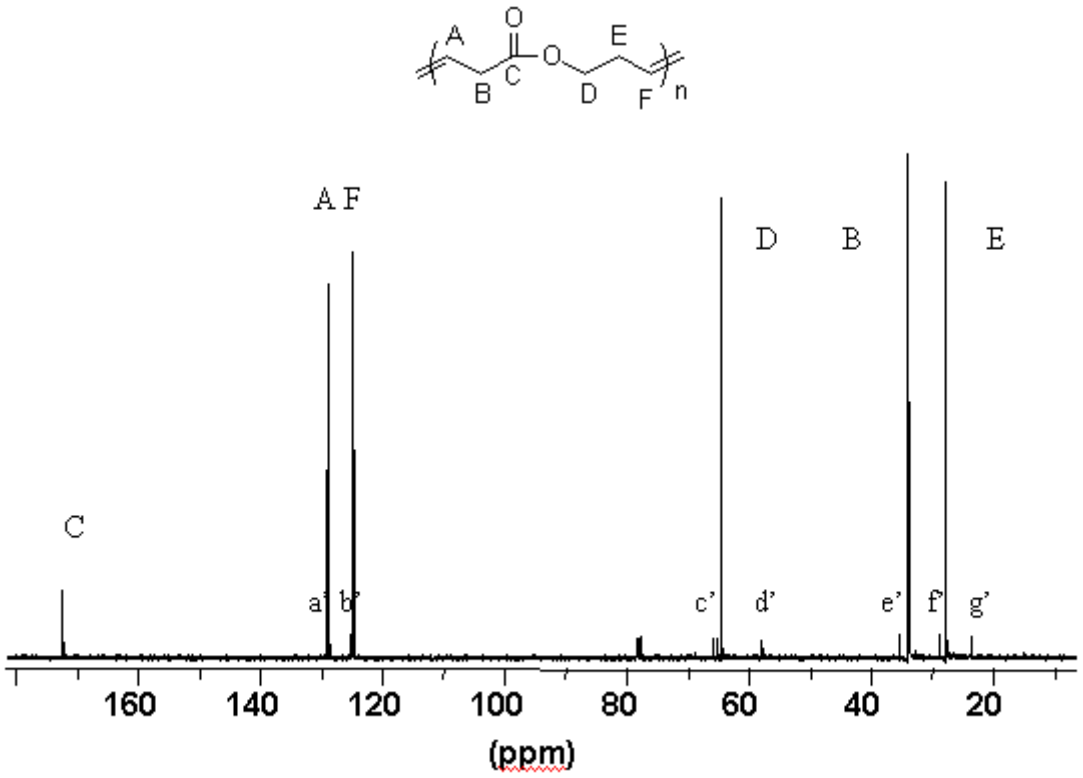


Fig. 4. ^{13}C spectrum of poly(DHO2) initiated by **1** in bulk at 60°C (2c in Tab. 2). Solvent: $CDCl_3$. Signals a' - g' refer to cyclics

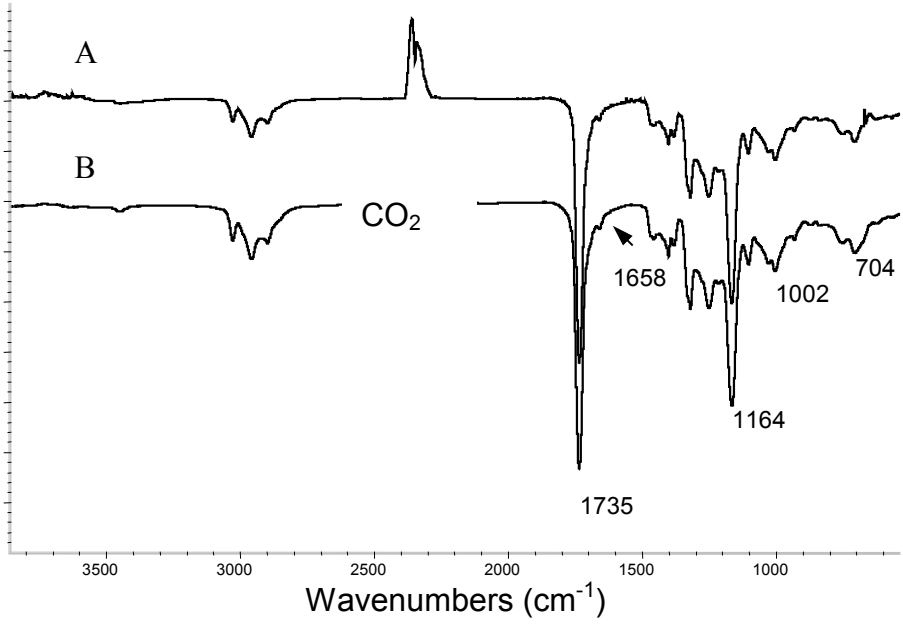


Fig. 5. FT-IR spectra of poly(DHO2) initiated by $Al(O^iPr)_3$ (A) and by **1** (B)

Tab. 3. Metathesis copolymerization of DHO2 initiated by Schrock's catalyst **1**

Entry	Comonomer	Catalyst in %	f_{DHO2} [a]	Time in h	Temp. in °C	Yield in %	F_{DHO2} [b]	$M_{n,SEC}$ [c] $\times 10^{-4}$	M_w/M_n
3a	NBE [d]	1.3	0.33	17	60	75	0.06	8.1	2.20
3b	CO [e]	1.5	0.19	24	60	80	0.06	12.8	5.3
3c	CO	1.5	0.32	24	60	70	0.14	8.6	3.8
3d	COD [f]	1.5	0.26	19	60	75	0.09	2.8	1.8

[a] Molar content of DHO2 in the comonomer feed. [b] Molar content of DHO2 in the copolymer (^{1}H NMR). [c] $M_{n,SEC}$ based on calibration with PSt standards. [d] Norbornene in toluene (1.5 M). [e] *cis*-Cyclooctene. [f] 1,5-Cyclooctadiene.

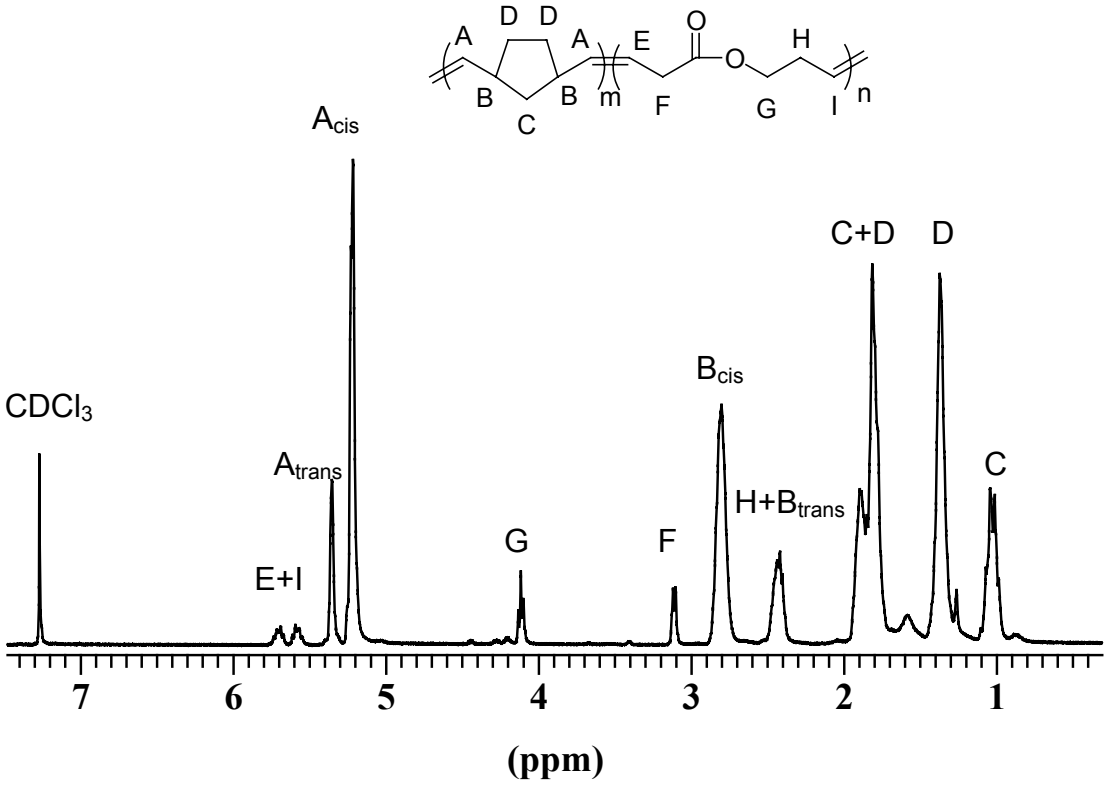


Fig. 6. ^{1}H NMR spectrum of the DHO2/norbornene copolymer (3a in Tab. 3). Solvent: $CDCl_3$

DHO2 has also been copolymerized successfully with monomers typically polymerized by ROMP, i.e., norbornene (NBE), *cis*-cyclooctene (CO), and 1,5-cyclooctadiene (COD). As shown in Tab. 3, when **1** is added to NBE/DHO2 mixtures in toluene at 60°C for 17 h, comonomer conversion is 75 %, and the ^{1}H NMR spectrum of the collected material (Fig. 6) shows the peaks characteristic of the DHO2 and NBE comonomer units, respectively. Nevertheless, the copolymer contains less DHO2 units than the comonomer feed, which indicates a lower reactivity for DHO2 compared to NBE. Copolymerization of DHO2 with *cis*-cyclooctene and 1,5-cyclooctadiene (COD) is also feasible in the bulk at 60°C, as confirmed by ^{1}H NMR analysis of the collected polymer (Fig. 7). Copolymer of high molecular weight can be

prepared although with a much higher polydispersity. In all the cases, the copolymer chains contain less DHO2 compared to the comonomer feed. Actually when catalyst **1** is added to, e.g., the DHO2/COD mixture, the reaction medium becomes highly viscous within 10 min at room temperature, as a result of the fast polymerization of COD as assessed by the ^{1}H NMR spectrum of the polymer recovered at this stage. Formation of a tapered diblock copolymer is therefore a reasonable hypothesis, that has been qualitatively assessed by selective degradation of the poly(DHO2) segments of copolymer 3d (Tab. 3) by HCl at 80°C. The polyester segments are totally degraded as confirmed by disappearance of the ^{1}H NMR resonances characteristic of poly(DHO2) (see Exptl. part). The apparent molecular weight is only slightly decreased (from 28 000 to 24 500) consistent with the small fraction of DHO2 co-units (9%) and a blocky structure of the copolymer.

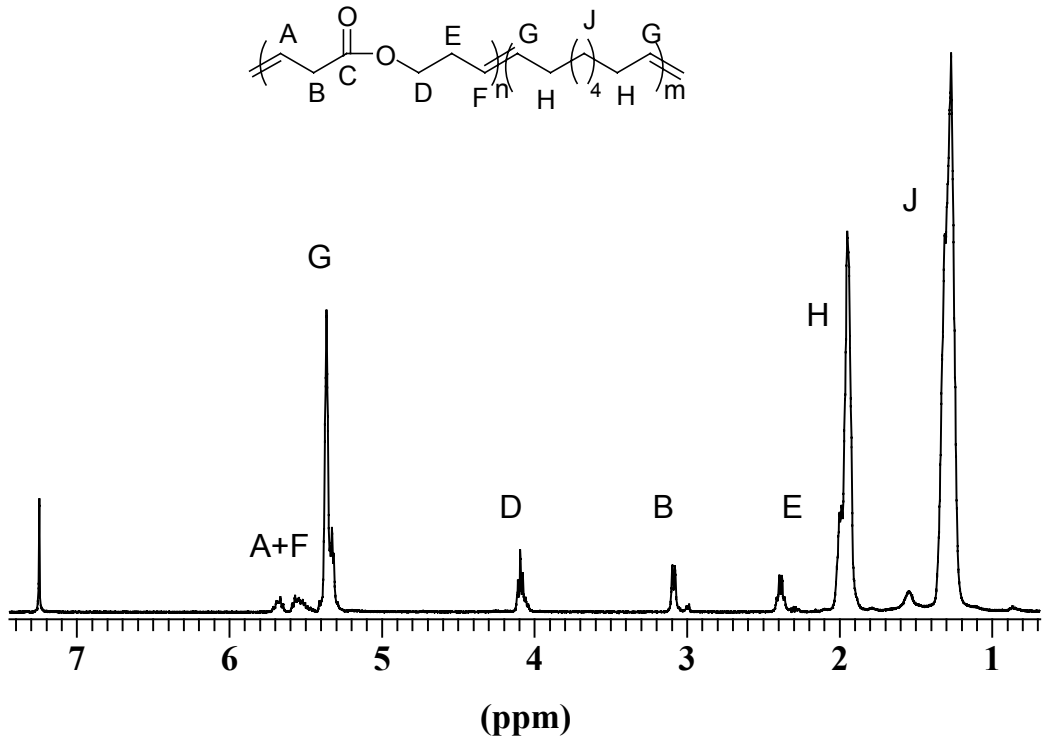


Fig. 7. ^{1}H NMR spectrum of the DHO2/*cis*-cyclooctene copolymer (3c in Tab. 3). Solvent: $CDCl_3$

It may be concluded that coordinative ROP and ROMP of DHO2 are polymerization mechanisms that complete each other. ROP initiated by $Al(O^iPr)_3$ must be carried out under dry conditions, whereas the metathesis initiator is not very sensitive to water. Homopoly(DHO2) with controlled low molecular weight (M_n < 20 000) and narrow molecular weight distribution is easily prepared by ROP at low temperature. Higher molecular weight poly(DHO2) of a broader molecular weight distribution is easily synthesized by ROMP. Furthermore, coordinative ring-opening copolymerization of DHO2 with other cyclic (di)esters is a way to incorporate double bonds into aliphatic polyesters, whereas metathesis copolymerization of DHO2 with cyclic olefins is a strategy to modify unsaturated polyolefins by inner ester groups sensitive to hydrolytic cleavage.

Conclusions

Coordinative ring-opening polymerization of DHO2 initiated by $Al(O^iPr)_3$ in toluene and ring-opening metathesis polymerization of the same monomer lead to unsaturated aliphatic polyesters of the same molecular structure. NMR analysis of the end-groups is consistent with a coordination-insertion mechanism for the coordinative process, which is better controlled at low temperature (0°C vs. 25°C). Metathesis polymerization of DHO2 initiated by Schrock's catalyst **1** in bulk at 60°C can lead to higher molecular weight homopolymer of higher polydispersity. Copolymerization of DHO2 with norbornene, *cis*-cyclooctene, and 1,5-cyclooctadiene leads to copolymers with a tapered diblock structure. From these preliminary experiments, it appears that copolymers with a more random structure could be prepared from appropriate comonomer feed composition (rich in DHO2) maintained constant during the whole process. Polyalkenamers could accordingly be made (bio)degradable, as a result of the ester co-units unstable towards (enzymatic) hydrolysis. This general strategy will be studied further, as an easy way to make the ROMP generated polymers (and their hydrogenated version) more environment-friendly and easily derivatized into telechelics.

Acknowledgement: The authors are indebted to "Services Féderaux des Affaires Scientifiques, Techniques et Culturelles" for general support to CERM in the frame of "PAI 4-11: Supramolecular Chemistry and Supramolecular catalysis".

[1] (a) Albertsson, A. C.; *J. Macromol. Sci., Pure Appl. Chem.* **1993**, *A30*, 757. (b) Ikada, Y.; Tsuji, H.; *Macromol. Rapid Commun.* **2000**, *21*, 117.

[2] Löfgren, A.; Albertsson, A. C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph.; *Macromolecules* **1994**, *27*, 5556.

[3] (a) Tian, D.; Dubois, Ph.; Jérôme, R.; *Macromolecules* **1997**, *30*, 1947. (b) Detrembleur, C.; Mazza, M.; Halleux, O.; Lecomte, Ph.; Mecerreyes, D.; Hedrick, J. L.; Jérôme, R.; *Macromolecules* **2000**, *33*, 14.

[4] Trollsas, M.; Lee, V. Y.; Mecerreyes, D.; Lowenhielm, P.; Moller, M.; Miller, R. D.; Hedrick, J. L.; *Macromolecules* **2000**, *33*, 4619.

[5] Liu, M.; Vladimirov, N.; Frechet, J. M.; *Macromolecules* **1999**, *32*, 6881.

[6] Mecerreyes, D.; Humes, J.; Miller, R. D.; Hedrick, J. L.; Detrembleur, C.; Lecomte, P.; Jérôme, R.; San Roman, J.; *Macromol. Rapid Commun.* **2000**, *21*, 779.

[7] Lou, X.; Detrembleur, C.; Lecomte, Ph.; Jérôme, R.; *Macromolecules* **2001**, *34*, 5806.

[8] (a) Detrembleur, C.; Mazza, M.; Lou, X.; Halleux, O.; Lecomte, Ph.; Jérôme, R.; *Macromolecules* **2000**, *33*, 7751. (b) Mecerreyes, D.; Miller, R. D.; Hedrick, J. L.; Detrembleur, C.; Jérôme, R.; *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 870.

[9] (a) Novak, B. M.; Risse, W.; Grubbs, R. H.; *Adv. Polym. Sci.* **1992**, *102*, 47. (b) Buchmeiser, M. R.; *Chem. Rev.* **2000**, *100*, 1565.

[10] Mecerreyes, D.; Dahan, D.; Lecomte, Ph.; Dubois, Ph.; Demonceau, A.; Noels, A. F.; Jérôme, R.; *J. Polym. Sci., Polym. Chem. Ed.* **1999**, *37*, 2447.

[11] Mecerreyes, D.; Lee, V.; Hawker, C. J.; Hedrick, J. L.; Wursch, A.; Volksen, W.; Magbitang, T.; Huang, E.; Miller, R. D.; *Adv. Mater.* **2001**, *13*, 204.

[12] Lou, X.; Jérôme, C.; Detrembleur, C.; Jérôme, R.; *Langmuir* **2002**, *18*, 2785.

[13] Lou, X.; Detrembleur, C.; Lecomte, Ph.; Jérôme, R.; *J. Polym. Sci., Polym. Chem. Ed.* **2002**, *40*, 2286.

[14] Lou, X.; Detrembleur, C.; Lecomte, Ph.; Jérôme, R.; *Macromol. Rapid Commun.* **2002**, *23*, 126.

[15] Dubois, Ph.; Jacobs, C.; Jérôme, R.; Teyssié, Ph.; *Macromolecules* **1991**, *24*, 2266.

[16] Dounis, P.; Feast, W. J.; Kenwright, A. M.; *Polymer* **1995**, *36*, 2787.

[17] Schwab, P.; Grubbs, R. H.; Ziller, J. W.; *J. Am. Chem. Soc.* **1996**, *118*, 100.