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Ring-Opening Polymerization of α -Chloro- ϵ -caprolactone and Chemical Modification of Poly(α -chloro- ϵ -caprolactone) by Atom Transfer Radical Processes

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ABSTRACT: A highly versatile strategy was implemented in order to attach a range of polymer grafts and functional groups along the backbone of poly(ϵ -caprolactone). α -Chloro- ϵ -caprolactone (α Cl ϵ CL) was first prepared by the Baeyer–Villiger oxidation of α -chlorocyclohexanone. This monomer (α Cl ϵ CL) was then copolymerized with ϵ -caprolactone in the presence of 2,2-dibutyl-2-stanna-1,3-dioxepane. Finally, the pendant activated chlorides of the copolymer were used to initiate (i) the “grafting from” of poly-(methyl methacrylate) by atom transfer radical polymerization and (ii) the grafting of benzoate groups by atom transfer radical addition of 3-butenyl benzoate.

Introduction

Nowadays, steadily increasing attention is paid to polymers that have potential as biomaterials and environmentally friendly materials.^{1,2} Among them, aliphatic polyesters have a leading position because of possible hydrolytic and/or enzymatic degradation into ultimately metabolized products in most cases. Lack of reactive groups (except for some end groups) is, however, a limitation to the fine-tuning of their properties and the extension of their application fields. Synthesis and (co)polymerization of cyclic (di)esters bearing a functional substituent, protected or not, is a very straightforward way toward reactive polyesters. Among the examples recently reviewed by some of us,² the synthesis and polymerization of γ -substituted- ϵ -caprolactone must be noted.

Aliphatic polyesters containing halogen,^{3,4} acid,^{5,6} alcohol,^{5–10} diol,⁵ ketal,^{11–14} ketone,¹⁵ carbon–carbon double bond,^{16–20} and amine⁵ have been prepared. The further chemical transformation of some of them has been successfully carried out in order to extend the range of the pendant functional groups, e.g., quaternization of bromides by pyridine²¹ and epoxidation,²¹ bromination,¹⁶ and hydrosilylation¹⁶ of unsaturations.

Recently, ROP has been combined with atom transfer radical techniques. Block copolymers consisting of one block prepared by ROP and a second block prepared by ATRP have been synthesized by initiating the copolymerization of a mixture of ϵ -caprolactone (ϵ CL) and methyl methacrylate MMA by 2,2,2-tribromoethanol, which is actually a dual initiator.^{22,23} Similarly, graft copolymers have been prepared in one step by copolymerizing a mixture of HEMA, MMA, and ϵ CL in the presence of 2,2-dichloroacetophenone.²³

Hedrick showed that γ -(ϵ -caprolactone) 2-bromo-2-dimethylpropionate is nothing but an inimer able to react as an initiator for atom transfer radical polymerization (ATRP) and as a monomer for ROP.²⁴ The ATRP of this inimer is an easy way to prepare macromonomers with a polymerizable ϵ -caprolactone head. Conversely, ROP leads to polyester with pendant activated bromide, well-suited to “grafting from” reaction by ATRP. Moreover, one example of atom transfer radical addition

(ATRA) of methyl methacrylate onto halogenated polyesters has been reported.²⁵

This paper aims at reporting on a straightforward route to a wide range of aliphatic polyesters in only three steps starting from α -chlorocyclohexanone. First, α -chloro- ϵ -caprolactone (α Cl ϵ CL) is prepared by the Baeyer–Villiger oxidation of α -chlorocyclohexanone. It may be noted that this monomer was previously reacted with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) with formation of easily polymerizable ϵ -caprolactone containing an endocyclic double bond in either the α or β position.¹⁹ In a second step, the ring-opening polymerization leads to poly(ϵ -caprolactone) α -substituted by chloro groups. Finally, the polymer can be used either as a macro-initiator for ATRP and synthesis of graft polyesters or as substrate for ATRA of an olefin substituted by a suitable functional group. This strategy is highly versatile because of the large variety of grafts and organic functions that can be attached to the polyester backbone.

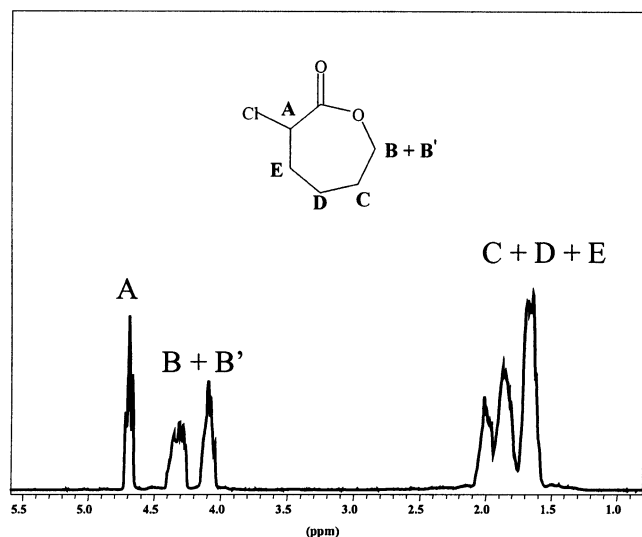
Experimental Section

Materials. α -Chlorocyclohexanone (Aldrich, 98%) and *m*-chloroperoxybenzoic acid (mCPBA) (Fluka, 70%), *N,N*-dimethylformamide (DMF) (Aldrich), 3-buten-1-ol (Aldrich), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (Aldrich) were used as received. Copper bromide (Aldrich) was recrystallized in glacial acetic acid. Tris[2-(dimethylamino)ethyl]amine (Me₆TREN) was prepared according to Ciampolini.²⁶ 2,2-Dibutyl-2-stanna-1,3-dioxepane (DSDOP) was prepared according to Kricheldorf.²⁷ The synthesis of α -chloro- ϵ -caprolactone was reported elsewhere.¹⁹ This lactone was dried by repeated (three times) azeotropic distillation of toluene just before polymerization. 3-Butenyl benzoate was prepared according to the Barrett procedure.²⁸ ϵ -Caprolactone (ϵ CL) (Janssen Chimica) and methyl methacrylate (MMA) (Aldrich) were dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use. Toluene was dried by refluxing over a benzophenone–sodium mixture and distilled under a nitrogen atmosphere.

Synthesis of α -Chloro- ϵ -caprolactone. 20 g (81 mmol) of mCPBA (70%) was added to a solution of 10 g (75 mmol) of 2-chlorocyclohexanone in 100 mL of dichloromethane at room temperature. After 96 h, the reaction flask was cooled to -20°C in order to precipitate *m*-chlorobenzoic acid. After filtration, the solution was washed with a saturated aqueous solution of

Table 1. Homopolymerization of $\alpha\text{Cl}\epsilon\text{CL}$ Initiated by DSDOP in Toluene at 20 °C

entry	monomer	$[\text{M}]_0/[\text{DSDOP}]_0$	time (min)	conv (%)	$M_{n,\text{th}}$ (g/mol)	$M_{n,\text{NMR}}$ (g/mol)	$M_{n,\text{SEC}}^a$ (g/mol)	M_w/M_n (SEC)
1	$\alpha\text{Cl}\epsilon\text{CL}$	16.9	90	100	2500	2400	2500	1.4
2	$\alpha\text{Cl}\epsilon\text{CL}$	33.8	90	100	5000	6000	6000	1.3
3	$\alpha\text{Cl}\epsilon\text{CL}$	67.6	10	89	9000	8000	8000	1.2

^a Calibration with polystyrene standards.**Figure 1.** ^1H NMR spectrum of $\alpha\text{Cl}\epsilon\text{CL}$.

NaHSO_3 (three times), with an aqueous solution of NaHCO_3 (three times), and finally with water. After drying over MgSO_4 , the organic phase was filtered, and the solvent was removed under reduced pressure. The residue was distilled under reduced pressure, and 9 g of α -chloro- ϵ -caprolactone (bp = 75–77 °C at 0.1 mmHg) was collected.

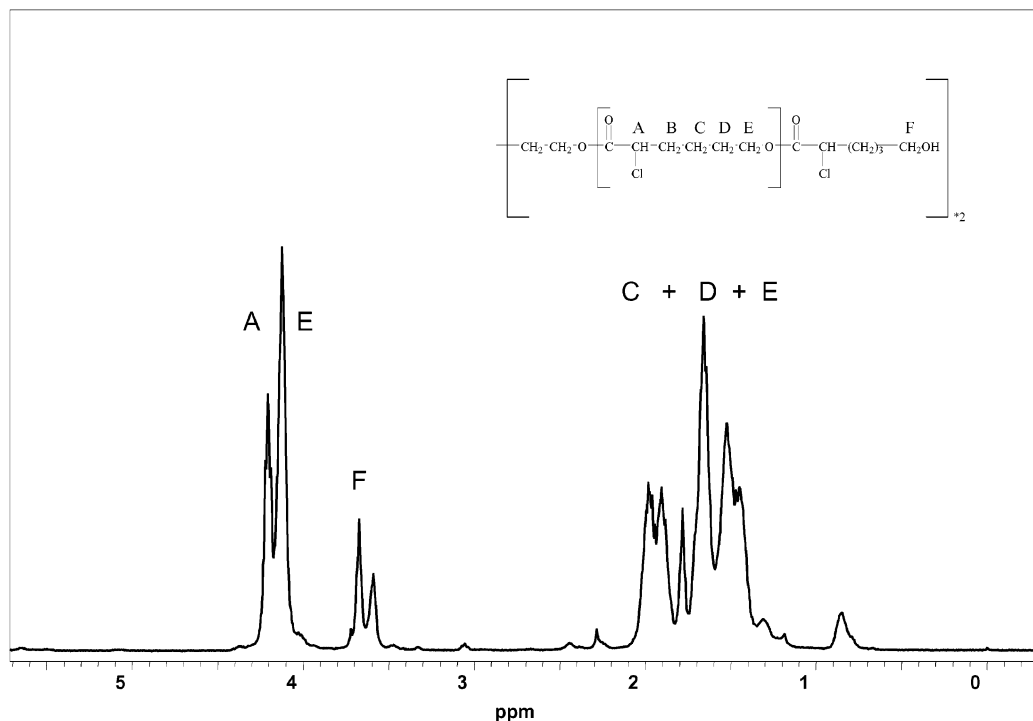
Polymerization Technique. Homopolymerization and random copolymerization were carried out at 20 °C in toluene. α -Chloro- ϵ -caprolactone was dried by repeated (three times) azeotropic distillation of toluene just before polymerization. Then, solvent, ϵ -caprolactone (for random copolymerization only), and initiator (DSDOP in toluene) were successively

added through a rubber septum with a syringe or a stainless steel capillary. After polymerization, an excess of 1 N HCl was added, and the polymer was recovered by precipitation in cold methanol.

Block copolymerization was carried out as follows. α -Chloro- ϵ -caprolactone polymerization was initiated by DSDOP. After 2 h, an aliquot of the polymerization medium was picked out, and poly(α -chloro- ϵ -caprolactone) (poly($\alpha\text{Cl}\epsilon\text{CL}$)) was deactivated and precipitated into cold methanol for analysis by size exclusion chromatography (SEC) and ^1H NMR. A known amount of a solution of ϵ -caprolactone in toluene was added to the “living” poly($\alpha\text{Cl}\epsilon\text{CL}$) solution. After conversion of ϵCL (2 h), an excess of 1 N HCl was added, and the copolymer was precipitated in cold methanol.

Synthesis of Graft Polyesters by ATRP. In a typical experiment, 0.25 g of poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) with a molar fraction of $\alpha\text{Cl}\epsilon\text{CL}$ ($F_{\alpha\text{Cl}\epsilon\text{CL}}$) = 0.03 (i.e., 0.07 mmol of pendant chlorides), 0.007 g of CuCl (0.07 mmol), and 0.002 g of CuCl_2 (0.014 mmol) were placed in a glass reactor filled with nitrogen. 2 mL of MMA (18.72 mmol), 0.2 mL of a HMTETA solution in toluene (0.35 M, 0.07 mmol), and 3 mL of toluene were added into a second flask under nitrogen and then transferred to the reactor. The ATRP was conducted at 80 °C. The copolymer was precipitated in heptane, kept at –20 °C overnight, and finally collected by filtration and evaporation of the liquid phase.

Transformation of Poly(α -chloro- ϵ -caprolactone) by ATRA. 1 g of poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) (0.0038 mol of pendant chlorides) and 0.54 g of CuBr (0.0038 mol) were added into a glass reactor that was air-evacuated and filled by nitrogen. 2.67 g of 3-butenyl benzoate (0.0152 mol), 0.8 mL of Me_6TREN , and 7 mL of DMF were then added in a second flask under nitrogen and then transferred to the reactor. ATRA was conducted at 60 °C for 90 min, and the copolymer was recovered as aforementioned.

**Figure 2.** ^1H NMR spectrum of poly($\alpha\text{Cl}\epsilon\text{CL}$).

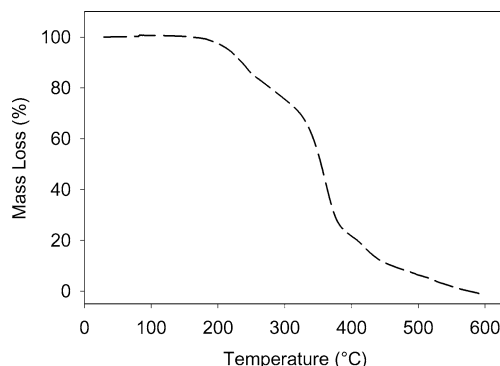


Figure 3. Thermogravimetric analysis of poly(α Cl ϵ CL).

Characterization. Size exclusion chromatography (SEC) was performed in THF at 40 °C with a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector. Columns HP PL gel 5 μ (10⁵, 10⁴, 10³, and 100 Å) were calibrated with polystyrene standards. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ 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, after heating the samples up to 100 °C and cooling to −80 °C. Thermograms were recorded during the second heating cycle at 10 °C/min.

Results and Discussion

Oxidation of α -chlorocyclohexanone by *m*-chloroperoxybenzoic acid results in a mixture of two isomeric lactones (α Cl ϵ CL/ ϵ Cl ϵ CL) in a 95/5 molar ratio. The isomers are easily separated by distillation under reduced pressure, and the major isomer, α Cl ϵ CL, is collected within a high yield (70%) and a high purity (>99%). Figure 1 shows the ¹H NMR spectrum for the

Table 2. Copolymerization of α Cl ϵ CL and ϵ CL Initiated by DSDOP

entry	$f_{\alpha\text{Cl}\epsilon\text{CL}}^a$ (%)	$F_{\alpha\text{Cl}\epsilon\text{CL}}^b$ (%)	conv (%)	$M_{n,\text{th}}^c$ (g/mol)	$M_{n,\text{NMR}}^d$ (g/mol)	$M_{n,\text{SEC}}^e$ (g/mol)	M_w/M_n (SEC)
1	3.3	3.3	100	13 000	13 500	29 000	1.5
2	10	12	100	10 000	13 000	29 000	1.5
3	25	29	100	10 000	9 500	20 500	1.4
4	44	48	88	9 000	9 000	14 000	1.4
5	50	49	100	10 000	11 700	13 000	1.4
6	62	68	100	10 000	8 500	9 000	1.2

^a Calculated by eq 6. ^b Calculated by eq 5. ^c Calculated by eq 3. ^d Calculated by eq 4. ^e Calibration with polystyrene standards.

purified α Cl ϵ CL. This monomer is thus easily prepared in one step from a commercially available compound on a multigram scale. This lactone can be stored at −20 °C for a few weeks without significant loss of polymerizability.

The molecular characteristics of poly(α -chloro- ϵ -caprolactone) samples, prepared by ROP initiated by 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) in toluene at 20 °C, from different monomer to DSDOP molar ratios, are shown in Table 1. Polymerizations are quantitative within less than 2 h, which is significantly faster than for ϵ CL polymerization. Indeed, a low conversion of 32% is observed for the ϵ CL polymerization at room temperature after 90 min. When α Cl ϵ CL is substituted for ϵ CL under the same conditions, a high conversion of 89% is observed after only 10 min (Table 1, entry 3). Thus, α -substitution of ϵ CL by an electron-withdrawing chlorine atom increases the polymerization rate. The molecular weight distribution of poly(α Cl ϵ CL) is narrow, which indicates a fast initiation compared to propagation and a fast propagation compared to transfer/termination reactions, if any. The ¹H NMR spectrum typical of poly(α Cl ϵ CL) (Figure 2) shows the major peaks characteristic of the polyester backbone and the hy-

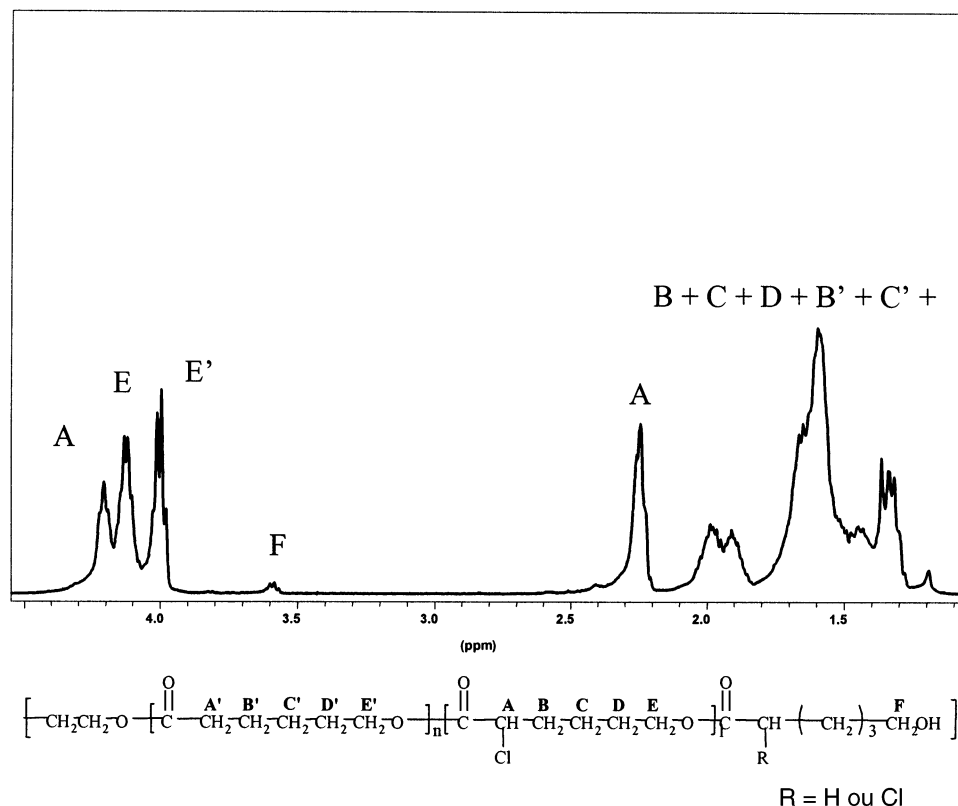


Figure 4. ¹H NMR spectrum of poly(α Cl ϵ CL-co- ϵ CL).

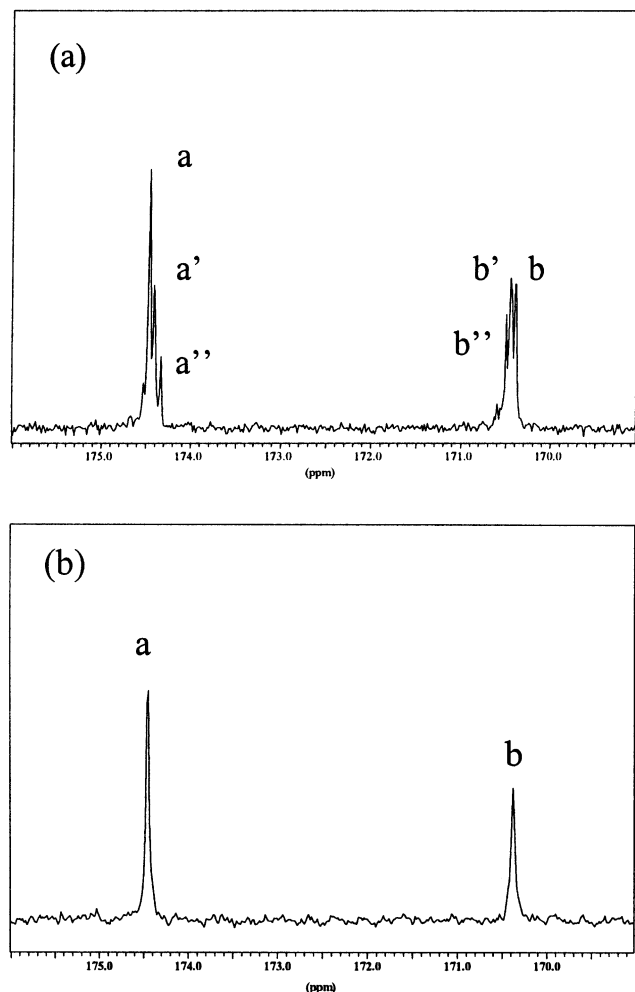


Figure 5. ^{13}C NMR spectrum in the carbonyl region of (a) poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) and (b) poly($\epsilon\text{CL-b-}\alpha\text{Cl}\epsilon\text{CL-b-}\epsilon\text{CL}$).

droxyl end group as well. A close agreement between the theoretical molecular weight calculated by eq 1 and the experimental value calculated from the relative intensity of the ^1H NMR resonances A–E (Figure 2) for the monomer unit and F for the end group (eq 2) is consistent with a well-controlled polymerization. It must be noted that, in contrast to poly(ϵCL), the molecular weight of poly($\alpha\text{Cl}\epsilon\text{CL}$) measured by ^1H NMR agrees with SEC data based on a calibration with polystyrene standards.

$$M_{n,\text{th}} = \frac{[\alpha\text{Cl}\epsilon\text{CL}]_0 \times 148 \times \text{conv}}{[\text{DSDOP}]_0} \quad (1)$$

$$M_{n,\text{NMR}} = \frac{4I_{\text{AE}} \times 148}{3I_{\text{F}}} \quad (2)$$

I_{AE} and I_{F} stand for the integral of the corresponding peaks assigned to the A,E and F protons, as shown in Figure 2.

Thermogravimetric analysis shows that the copolymer is thermally stable up to 200 °C (Figure 3). Then, a three-step thermal decomposition is noted, the two last steps being observed for neat PCL in the same temperature range.²⁹ The first step at 200 °C is thus typical of the chloride substitution of ϵCL . A more detailed investigation is however required to elucidate the underlying mechanism.

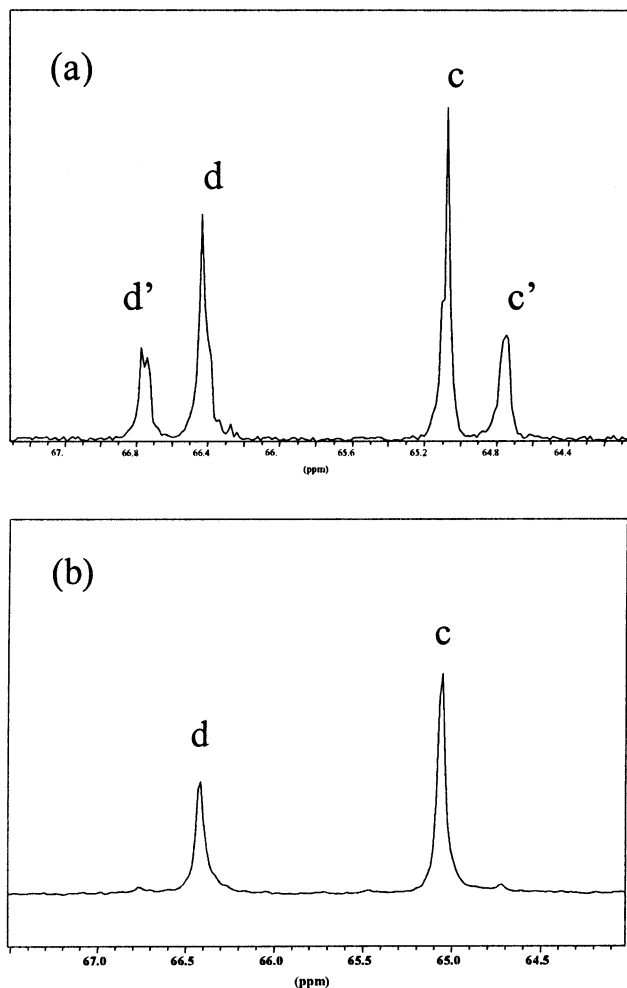


Figure 6. ^{13}C NMR spectrum in the $-\text{OCH}_2-$ region of (a) poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) and (b) poly($\epsilon\text{CL-b-}\alpha\text{Cl}\epsilon\text{CL-b-}\epsilon\text{CL}$).

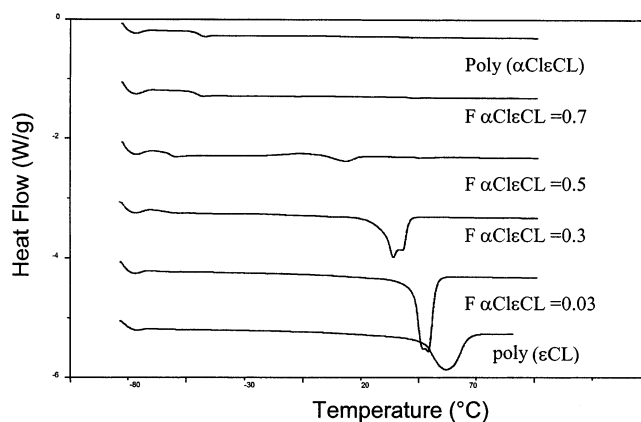


Figure 7. DSC thermograms of poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) with different composition.

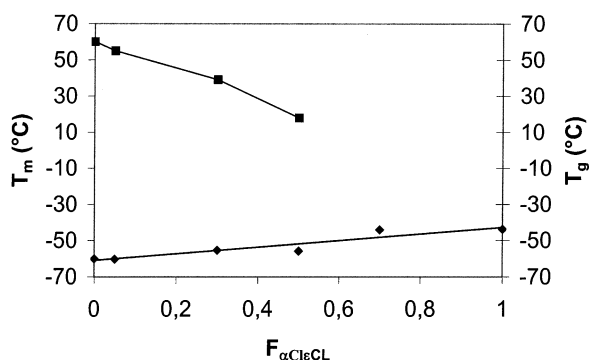
The molecular characteristics of the random copolymers of α -chloro- ϵ -caprolactone and ϵ -caprolactone synthesized in this work are shown in Table 2. Figure 4 shows the ^1H NMR spectrum for a poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) copolymer. The theoretical molecular weights (eq 3) agree with the values measured by ^1H NMR (eq 4). The molecular weight distribution estimated by SEC is in line with the reported values for the polymerization initiated by DSDOP. The molar composition of the copolymers ($F_{\alpha\text{Cl}\epsilon\text{CL}}$) measured by ^1H NMR (eq 5) agrees with the composition ($f_{\alpha\text{Cl}\epsilon\text{CL}}$) of the comonomer feed (eq 6). All in these data support that the random copoly-

Table 3. Sequential Copolymerization of α Cl ϵ CL and ϵ CL Initiated by DSDOP

macroinitiator poly(α Cl ϵ CL)				triblock poly(ϵ CL- <i>b</i> - α Cl ϵ CL- <i>b</i> - ϵ CL)			
$M_{n,th}$ (g/mol)	$M_{n,NMR}^a$ (g/mol)	$M_{n,SEC}$ (g/mol)	M_w/M_n (SEC)	$M_{n,th}$ (g/mol)	$M_{n,NMR}^b$ (g/mol)	$M_{n,SEC}$ (g/mol)	M_w/M_n (SEC)
5000	4500	4400	1.5	10000	12000	21000	1.5

^a Calculated by eq 2. ^b Calculated by eq 4.**Table 4. Synthesis of Poly(α Cl ϵ CL-*co*- ϵ CL)-*g*-polyMMA Graft Copolymers by ATRP**

poly(α Cl ϵ CL- <i>co</i> - ϵ CL)				poly(α Cl ϵ CL- <i>co</i> - ϵ CL)- <i>g</i> -polyMMA				
M_n (SEC)	M_w/M_n (SEC)	conv (%)	f^a	$M_{n,th}$ PMMA grafts	M_n^b PMMA grafts (SEC)	M_w/M_n PMMA grafts (SEC)	M_n^c graft copolymer	M_w/M_n graft copolymer (SEC)
13000	1.5	56	0.4	11200	29000	1.5	110000	2.0

^a Initiator efficiency calculated by eq 8. ^b Determined after acidic hydrolysis of the polyester backbone; calibration with PMMA standards.^c Calculated by eq 9.**Figure 8.** Dependence of T_g and T_m measured by DSC with the molar content of ϵ CL in the copolymer ($F_{\epsilon CL}$).

merization of α Cl ϵ CL with ϵ CL is well controlled.

$$M_{n,th} = \frac{([\alpha Cl \epsilon CL]_0 \times 148) + ([\epsilon CL]_0 \times 114)}{[DSDOP]_0} \times \text{conv} \quad (3)$$

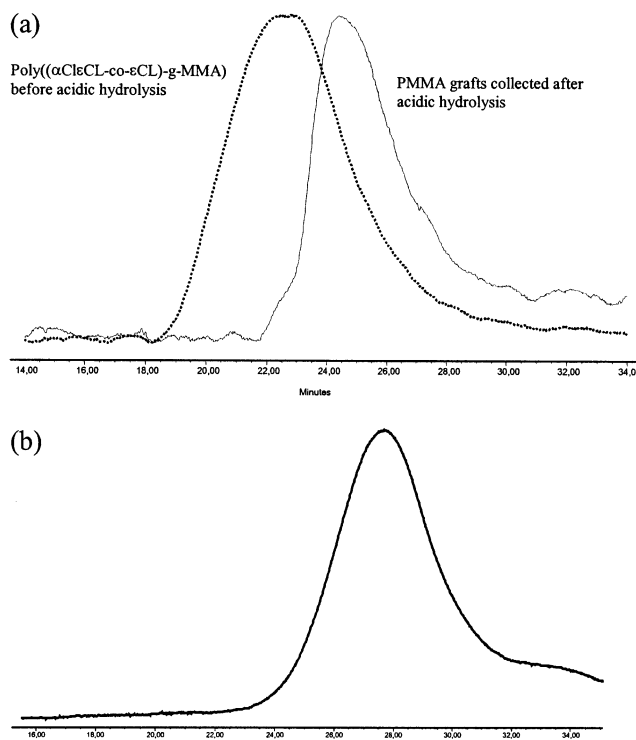
$$M_{n,NMR} = \frac{(\frac{1}{3}[I_{AEE'} - I_{A'}] \times 148) + (\frac{1}{2}I_{A'} \times 114)}{\frac{1}{4}I_F} \quad (4)$$

$$F_{\alpha Cl \epsilon CL} = \frac{\frac{1}{3}[I_{AEE'} - I_{A'}]}{(\frac{1}{3}[I_{AEE'} - I_{A'}] + \frac{1}{2}I_{A'}} \quad (5)$$

$$f_{\alpha Cl \epsilon CL} = \frac{[\alpha Cl \epsilon CL]_0}{[\alpha Cl \epsilon CL]_0 + [\epsilon CL]_0} \quad (6)$$

$I_{AEE'}$, $I_{A'}$, and I_F stand for the integral of the corresponding peaks assigned to the A, A', E, E', and F protons, as shown in Figure 4.

Figure 5 shows the carbonyl region of the ^{13}C NMR spectrum of a random copolymer, in which triads are observed. Peaks a and b are characteristic of the homotriads C-C-C and ClC-ClC-ClC, where C stands for ϵ CL and α Cl ϵ CL. This assignment is in agreement with the chemical shifts reported for the parent homopolymers poly(ϵ CL) and poly(α Cl ϵ CL). The additional peaks, a', a'', b', and b'', in the carbonyl region thus refer to the heterotriads and confirm the randomness of the copolymer. Figure 6 shows the same analysis for the methylene -CH₂-O- region. Four peaks are observed, consistent with diads. Peaks c and d correspond to the C-C and ClC-ClC homodiads, and the additional peaks c' and d' are assigned to the ClC-C heterodiads.

**Figure 9.** (a) SEC traces of poly(α Cl ϵ CL-*co*- ϵ CL)-*g*-MMA and PMMA grafts collected after the acidic hydrolysis of the polyester backbone. (b) SEC trace of poly(α Cl ϵ CL-*co*- ϵ CL) after ATRP of 2-butenyl benzoate.

The ϵ CL/ α Cl ϵ CL random copolymers have been analyzed by differential scanning calorimetry (DSC) (Figure 7). Copolymerization of ϵ CL with increasing amounts of α Cl ϵ CL has a strong effect on the thermal transitions (Figure 8). Poly(ϵ CL) shows indeed a T_g at -61°C and a melting temperature (T_m) at 57°C , whereas the chlorinated polyester (poly(α Cl ϵ CL)) is amorphous with a T_g at -44°C . T_m of poly(ϵ CL) decreases upon increasing α Cl ϵ CL content until $F_{\alpha Cl \epsilon CL} = 0.5$. Beyond this α Cl ϵ CL content, the copolymers are amorphous. Consistent with the miscibility of the amorphous phase of the two constitutive polyesters, only one T_g is observed which is intermediate between T_g 's for each parent homopolymer.

Finally, a triblock copolymer of ϵ CL and α Cl ϵ CL has been prepared by sequential polymerization of ϵ CL and α Cl ϵ CL. First, the α Cl ϵ CL polymerization has been initiated at room temperature by DSDOP, followed by the addition of ϵ CL at 0°C . The experimental molecular weight for each block is in agreement with the value

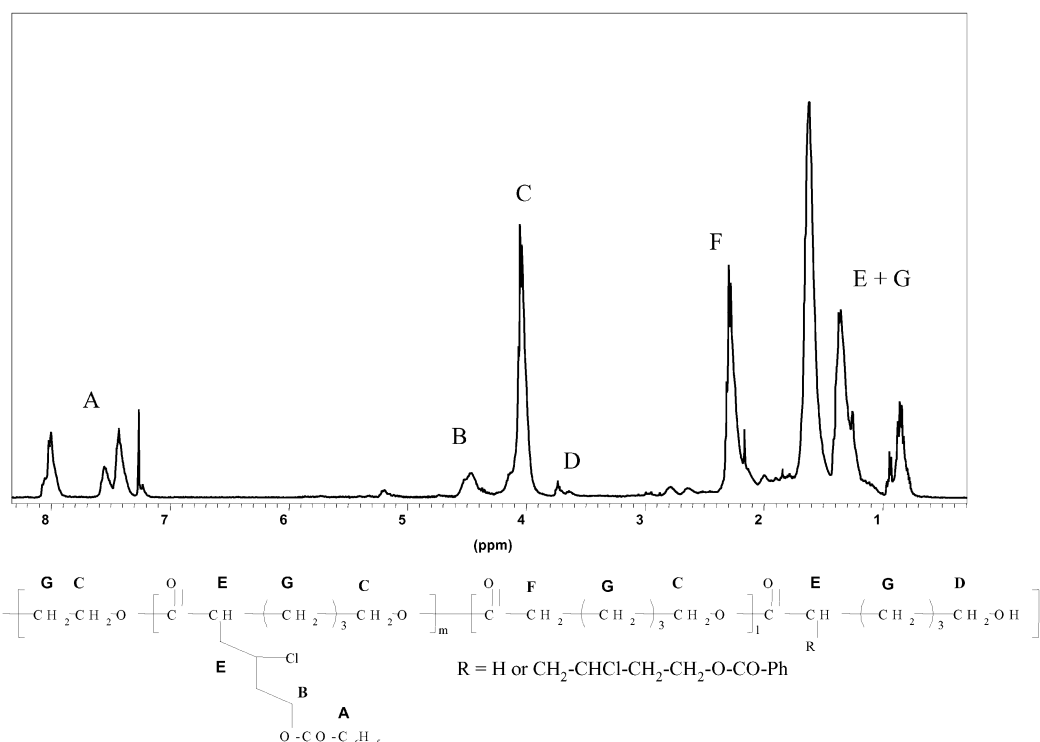


Figure 10. ^1H NMR of poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) after ATRA of 3-butenyl benzoate.

expected for a living polymerization at complete monomer conversion (Table 3).

To confirm that the blockiness of the copolymer has not been affected by any transesterification reaction, the ^{13}C NMR spectrum has been recorded. Indeed, the occurrence of transesterification reactions must result in mixed sequences easily detected by additional resonances in the carbonyl region. Figures 5b and 6b show only one peak characteristic of each homopolymer and no heterodiad peak, consistent with the expected sequential structure.

The poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) copolymer is a potential macroinitiator for the CuCl/HMTETA-mediated ATRP for the synthesis of graft copolymers. Table 4 shows the results of the ATRP grafting of poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) by MMA ($F_{\alpha\text{Cl}\epsilon\text{CL}} = 0.10$; $M_{n,\text{NMR}} = 13\,000$).

$$M_{n,\text{PMMA,th}} =$$

$$\frac{[\text{MMA}]_0 \times 100}{\text{DP}_{\text{poly}(\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL})} \times F_{\alpha\text{Cl}\epsilon\text{CL}} \times [\text{poly}(\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL})]_0} \quad (7)$$

The SEC trace shows an expected shift to higher apparent molecular weight. To confirm the grafted structure of the copolymer, the polyester backbone has been degraded in acidic medium (1,4-dioxane/HCl 37 wt %, 85 °C, 72 h), and the grafts have been recovered by precipitation and directly analyzed by SEC, as shown in Table 4 and Figure 9a. The molecular weight measured by SEC for the PMMA grafts is an absolute value because of the use of universal calibration. The initiation efficiency f has been calculated from the comparison of the experimental M_n and the theoretical value (eq 7) for the PMMA grafts (eq 8). The molecular weight of the graft copolymer has been calculated by eq 9, where DP stands for the degree of polymerization. The DSC thermogram of poly($(\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL})$ -g-MMA) shows one T_g at 105 °C characteristic of the PMMA grafts and

one T_m at 50 °C ($\Delta H = 0.34$ J/g) for the poly(ϵCL) backbone.

$$f = \frac{M_{n,\text{PMMA,th}}}{M_{n,\text{PMMA,SEC}}} \quad (8)$$

$$M_{n,\text{graft copolymer}} = (M_{n,\text{PMMA}} \times \text{DP}_{\alpha\text{Cl}\epsilon\text{CL}} \times f) + M_{\text{macroinitiator}} \quad (9)$$

Poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) ($F_{\alpha\text{Cl}\epsilon\text{CL}} = 0.53$; $M_n(^1\text{H NMR}) = 12\,000$; $M_n(\text{SEC}) = 16\,000$; $M_w/M_n = 1.5$) has also been reacted with 3-butenyl benzoate in *N,N*-dimethylformamide (DMF) at 60 °C, using CuBr/tris[2-(dimethylamino)ethyl]amine (Me_6TREN) as an ATRP catalyst. After 90 min, the polymer was precipitated and analyzed by ^1H NMR, as shown in Figure 10. The signals associated with the $-\text{CO}-\text{CHCl}-$ units have disappeared, and the observation of peaks in the aromatic region is an unambiguous evidence for the completeness of the reaction. The SEC analysis is shown in Figure 9b ($M_n(\text{SEC}) = 20\,000$). No change in polydispersity is noted, which strongly suggests that no significant chain degradation has occurred.

Conclusions

A three-step strategy has been reported for the synthesis of new aliphatic polyesters. In the first step, $\alpha\text{Cl}\epsilon\text{CL}$ has been prepared by Baeyer–Villiger oxidation of α -chlorocyclohexanone. $\alpha\text{Cl}\epsilon\text{CL}$ homopolymerization and random and block copolymerization of $\alpha\text{Cl}\epsilon\text{CL}$ and ϵCL have been successfully initiated by DSDOP. The tuning of the initiator to monomer molar ratio is a tool to control the molecular weight. It must be pointed out that $\alpha\text{Cl}\epsilon\text{CL}$ polymerizes much more rapidly than ϵCL and that the molecular weight distribution of poly($\alpha\text{Cl}\epsilon\text{CL}$) is therefore narrower compared to that of poly(ϵCL). The last step relies on ATRA or ATRP processes. Indeed, poly($\alpha\text{Cl}\epsilon\text{CL-co-}\epsilon\text{CL}$) is an efficient mac-

roinitiator for ATRP of e.g. MMA, as a route to graft copolymers consisting of biodegradable polyester backbone and e.g. PMMA grafts. 3-Butenyl benzoate has been shown to react with poly(α Cl ϵ CL-co- ϵ CL) according to an ATRA mechanism without any significant degradation. This modified copolymer is amorphous and shows a glass transition at -50°C . This ATRA reaction is currently extended to olefins containing other functional groups, such as alcohol, carboxylic acid, epoxide, and amine, with the purpose to make functionalized aliphatic polyesters available.

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