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Functionalization of poly(ε-caprolactone) by pendant hydroxyl, carboxylic acid and epoxide groups by atom transfer radical addition

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Abstract

A straightforward strategy is proposed for grafting hydroxyl, carboxylic acid and epoxide groups along poly(ε-caprolactone) chains. Statistical copolymerization of ε-caprolactone (εCL) with α-chloro-ε-caprolactone (αClεCL) has been initiated by 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP), followed by the atom transfer radical addition (ATRA) of but-3-en-1-ol, vinylacetic acid and 1,2-epoxyhex-5-ene, respectively, onto the α-chloro units of a poly(αClεCL-*co*-εCL) copolymer. αClεCL is easily prepared by the Baeyer–Villiger oxidation of 2-chlorocyclohexanone. The influence of the experimental conditions, i.e. temperature, solvent, catalyst, on the grafting yield has been discussed. Because ATRA is tolerant of the investigated functional groups, no protection/deprotection reaction is required, which is a major advantage of the method.

Keywords: Atom transfer radical addition; Aliphatic polyesters; Poly(ε-caprolactone)

1. Introduction

At the time being, a steadily increasing attention is paid to new biomaterials and environmentally friendly thermoplastics, which accounts for the unique position and role of biodegradable and biocompatible aliphatic polyesters [1]. Among then, poly(ε-caprolactone) (PCL) is made available to the market place by Solvay (CAPA®), Union Carbide (Tone®) and Daicel (Celgreen®). A major limitation to the use of PCL, and other aliphatic polyesters, is the lack of pendant functional groups along the chains, which prevents reactive groups from providing the related materials with specific functionalities.

Recently, two main strategies have been reported for the synthesis of functional groups containing aliphatic polyesters. In the first approach, PCL is reacted with lithium amides with formation of a poly(enolate), which is then reacted with an appropriate electrophile [2]. The problem is the unavoidable degradation of the polyester chains by the nucleophilic sites. The second strategy relies on the ring-opening polymerization (ROP) of ε-caprolactone substituted, mainly in γ-position, by various functional groups, e.g. acrylate [3], protected carboxylic acid [4,5], protected alcohol [6], ketal [7], ketone [8] and halogen [9,10]. A limitation may, however, be found in the limited yield of a multi-step process. Moreover, aluminum and tin alkoxides-mediated ROP is not tolerant of hydroxyl, carboxylic acid and epoxy groups. In these specific cases, hydroxyl and carboxylic acid groups must be protected before ROP and deprotected afterwards [4–6], whereas post-polymerization epoxidation has to be considered for grafting epoxides along the chains [11–13]. For all these reasons, straightforward strategies are highly desirable to prepare aliphatic polyesters with pendant hydroxyl, carboxylic acid and epoxide groups, respectively.

Substitution of radical species for the anionic ones used in the 'poly(enolate)' strategy is an alternative worth being tested, because of the much higher tolerance of the aliphatic polyesters of radicals compared to nucleophiles [2]. Hedrick et al. synthesized and polymerized γ-(2-bromo-2-dimethyl-propionate)-ε-caprolactone, and they reported one example of atom transfer radical addition (ATRA) of methyl methacrylate onto the parent polymer [14]. This report prompted us to investigate further the functionalization of

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the PCL backbone by ATRA of a broader range of vinylic compounds, merely because hydroxyl, carboxylic acid and epoxy groups are of a limited sensitivity to radical species, which allows them to be grafted without any cumbersome protection/deprotection reactions.

In a previous paper, we showed that γ-(2-bromo-2-dimethylpropionate)-ε-caprolactone could be advantageously replaced by α-chloro-ε-caprolactone, because of a one-step synthesis by Baeyer–Villiger oxidation of the commercially available 2-chlorocyclohexanone [15]. Moreover, ATRA of 3-butenyl benzoate onto poly(α-chloro-ε-caprolactone-*co*-ε-caprolactone) was reported to be mediated by CuBr/Me_6-Tren catalyst in *N*,*N*-dimethylformamide [15].

This paper aims at reporting on the grafting of poly(α-chloro-ε-caprolactone-*co*-ε-caprolactone) by 3-buten-1-ol, vinylacetic acid, 1,2-epoxyhex-5-ene (Fig. 1). These terminal olefins cannot be polymerized by ATRP, only a single addition can take place by an ATRA mechanism. The influence of the experimental conditions, i.e. solvent, temperature, copper catalyst, on the grafting efficiency will be discussed.

2. Experimental

2.1. Materials

Toluene (Chem-lab), *N*,*N*-dimethylformamide (DMF) (Aldrich), 3-buten-1-ol (Aldrich), vinylacetic acid (Aldrich), 1,2-epoxyhex-5-ene (Aldrich), acetic acid (Aldrich), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (Aldrich) were used as received. Copper bromide (Aldrich) was recrystallized in glacial acetic acid. 2,2-Dibutyl-2-stanna-1,3-dioxepane (DSDOP) was prepared as reported elsewhere by Kricheldorf [16]. Synthesis of tris[2-(dimethylamino)ethyl]amine (Me_6-Tren) [17], α-chloro-ε-caprolactone (αClεCL) [11] and 3-butenyl benzoate [18] was also reported elsewhere. αClεCL was dried by repeated (three times) azeotropic distillation of toluene just before polymerization. ε-Caprolactone (εCL) (Janssen Chimica) was 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 nitrogen atmosphere.

2.2. Copolymerization

Random copolymerization was carried out at 20 °C in toluene in a previously dried glass reactor. 2.5 g (17 mmol) of α-chloro-ε-caprolactone, 1.9 ml (17 mmol) ε-caprolactone, 5 ml toluene and 3 ml initiator (0.15 M DSDOP in toluene) were sequentially added to the reactor through a rubber septum with a syringe or a stainless steel capillary. After 2 h of polymerization, an excess of 1 N HCl was added, and the copolymer was recovered by precipitation in cold heptane.

2.3. Chemical modification of poly(α-chloro-ε-caprolactone) by ATRA

one gram of poly(αClεCL-*co*-εCL) (0.0038 mol of pendant chloride), and 0.54 g of CuBr (0.0038 mol) were added into a glass reactor. The mixture was placed under vacuum for 5 min in order to get rid of oxygen. The reactor was then filled with nitrogen. 0.0152 mol of olefin, 0.87 g of Me_6-Tren or HMTETA (0.0038 mol) and 7 ml of DMF were then added in a second flask, degassed by bubbling of nitrogen for 10 min and then transferred to the reactor with a stainless steel capillary. ATRA was conducted at 60 °C, and the copolymer was recovered as aforementioned.

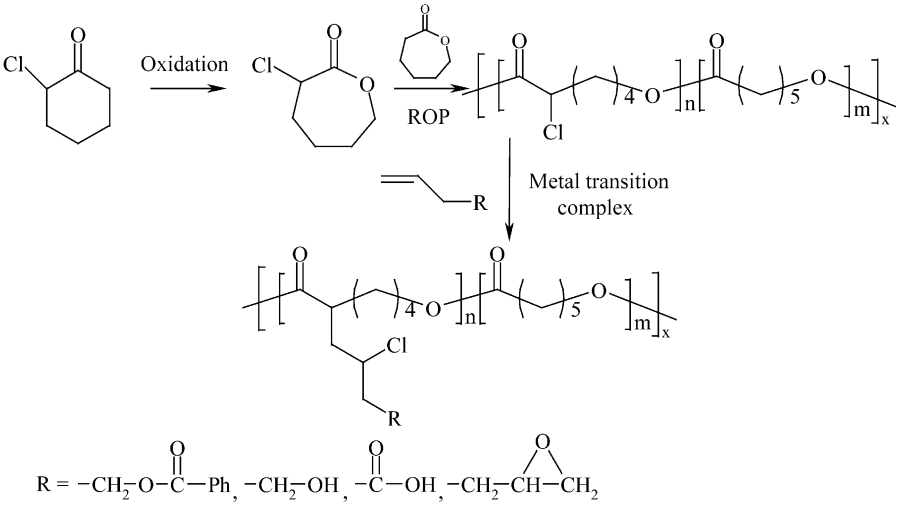

Fig. 1. General scheme for the functionalization of PCL by ATRA.

2.4. Characterization

Size exclusion chromatography (SEC) was performed in THF at 45 °C with a Waters liquid chromatograph equipped with a Waters refractive index detector. Columns HP PL gel 5 μm (10^5, 10^4, 10^3, 100 Å) were calibrated with polystyrene standards. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz in the FT mode with a Brucker AN 400 apparatus at 25 °C. Thermal gravimetric analysis (TGA) was carried out with a TA TGA Q500. Differential scanning calorimetry (DSC) was carried out with a TA DSC Q100 thermal analyzer calibrated with indium. Glass transition and melting temperatures were measured, after a first cooling (−80 °C) and heating (100 °C) cycle. Thermograms were recorded during the second heating cycle at 10 °C/min.

3. Results and discussion

3.1. Grafting of hydroxyl groups onto PCL

Statistical copolymerization of α-chloro-ε-caprolactone and ε-caprolactone (poly(αClεCL-*co*-εCL)) was initiated by 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) in toluene at 20 °C, as reported elsewhere [15]. A poly(αClεCL-*co*-εCL) copolymer of $M_n = 11{,}500$ g/mol and $M_w/M_n = 1.6$ was accordingly synthesized with an αClεCL molar fraction of 0.49. This copolymer was used in all the grafting experiments by ATRA reported in this work.

In a previous work, copper bromide was ligated by either HMTETA or Me_6-Tren and used as catalyst in the ATRP of MMA and the ATRA of 3-butenyl benzoate onto poly (αClεCL-*co*-εCL) [15]. Thus, 3-buten-1-ol has been first reacted with the activated chloride units of the poly (αClεCL-*co*-εCL) copolymer, in the presence of either CuBr/HMTETA or CuBr/Me_6-Tren. Whenever toluene is the solvent, the ATRA reaction does not take place whatever the ligand (Table 1, entries 1 and 2). This observation is surprising because the activated chloride of poly(αClεCL-*co*-εCL) was reported to initiate the ATRP of methyl methacrylate with the same catalysts in toluene [15]. Nevertheless, a survey of the literature shows that ATRA and ATRP can be mediated by the same catalyst to quite a different extent [19]. According to Vairon et al., substitution of *N*,*N*-dimethylformamide (DMF) for toluene is very effective in increasing the ATRP kinetics [20]. To the best of our knowledge, the origin of this remarkable solvent effect is not fully understood. Among other effects, copper complexes are much more soluble in DMF than in toluene, which allows ATRP to be performed under homogeneous conditions in this solvent with a favorable impact on the kinetics. Moreover, DMF is a potential ligand for Cu cations, which may also change the catalyst activity. Whatever the reasons for the beneficial effect of DMF, ATRA of 3-buten-1-ol onto the copolymer has been repeated in DMF at 60 °C. Under these conditions, the radical addition takes place, although with an efficiency that depends on the ligand. At constant time (4 h), temperature (60 °C) and number of 3-buten-1-ol equivalents (4) with respect to the activated chloride, the pendant chloride conversion is much higher with Me_6-Tren (95%) than with HMTETA (40%) (Table 1, entries 3 and 4). In addition to the ligand, the excess of 3-buten-1-ol has a decisive effect. Indeed, when the number of olefin equivalents is decreased from 4 to 2, the progress of the olefin addition decreases significantly as confirmed by entries 3 and 5 in Table 1.

Fig. 2 shows the ^{1}H NMR spectrum for the poly(αClεCL-*co*-εCL) copolymer after addition of 3-buten-1-ol. The assignment of the signals is shown in Fig. 2. The vinyl protons at 5.1 and 5.8 ppm have disappeared. Signals at 2.8, 3.6 and 3.8 ppm are typical of the grafted group. Pendant chloride conversions reported in Table 1 have been calculated according to Eqs. (1)–(3) where F_{ATRA} and $F_{\alpha ClεCL}$ stand for the molar content of the units grafted by ATRA and the unreacted α-chlorinated units, respectively. I stands for the integral of the ^{1}H NMR

Table 1
Influence of the catalyst, solvent and time on ATRA of 3-buten-1-ol onto the poly(αClεCL-*co*-εCL) copolymer at 60 °C

	Olefin	Catalyst	Solvent	[Olefin]/[pendant Cl groups]	Time (h)	Pendant chloride conversion (%)
1	3-Buten-1-ol	CuBr/Me_6-Tren	Toluene	4	24	0
2	3-Buten-1-ol	CuBr/HMTETA	Toluene	4	24	0
3	3-Buten-1-ol	CuBr/Me_6-Tren	DMF	4	4	>95
4	3-Buten-1-ol	CuBr/HMTETA	DMF	4	4	40
5	3-Buten-1-ol	CuBr/Me_6-Tren	DMF	2	4	33
6	3-Buten-1-ol	CuBr/HMTETA	DMF	2	8	37
7	Vinylacetic acid	CuBr/Me_6-Tren	DMF	4	4	0
8	Vinylacetic acid	CuBr/HMTETA	DMF	2	24	32
9	1,2-Epoxyhex-5-ene	CuBr/Me_6-Tren	DMF	4	4	n.d.
10	1,2-Epoxyhex-5-ene	CuBr/HMTETA	DMF	2	8	42

n.d., not determined because of cross-linking.

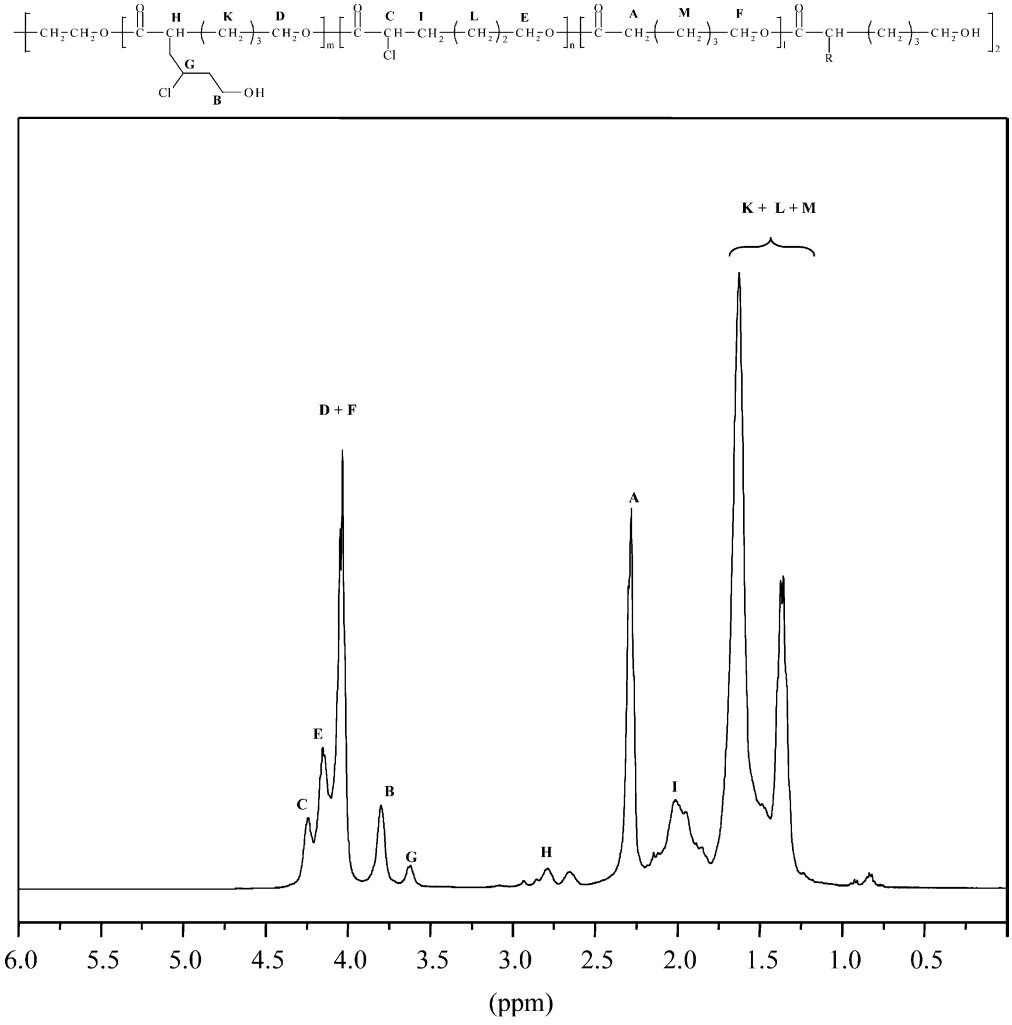

Fig. 2. ^{1}H NMR spectrum for the poly(αClεCL-*co*-εCL) copolymer added with 3-buten-1-ol.

peaks assigned in Fig. 2.

$$F_{\mathrm{ATRA}} = \frac{I_{\mathrm{B}}/2}{I_{\mathrm{B}}/6 + I_{\mathrm{A}}/6 + I_{\mathrm{C,D,E,F}}/3} \quad (1)$$

$$F_{\alpha\mathrm{Cl}\varepsilon\mathrm{CL}} = \frac{(I_{\mathrm{C,D,E,F}} - I_{\mathrm{B}} - I_{\mathrm{A}})/3}{I_{\mathrm{B}}/6 + I_{\mathrm{A}}/6 + I_{\mathrm{C,D,E,F}}/3} \quad (2)$$

$$\text{Conversion}\ (\%) = \frac{F_{\mathrm{ATRA}}}{F_{\mathrm{ATRA}} + F_{\mathrm{F}\alpha\mathrm{Cl}\varepsilon\mathrm{CL}}} \times 100 \quad (3)$$

When ATRA mediated by CuBr/HMTETA is performed at 85 °C for 24 h, the apparent molecular weight of the chains decreases from 11,500 to 3500. In order to know whether this degradation results, at least partly, from transesterification reactions initiated by hydroxyl groups, ATRA at 85 °C has been repeated with 3-buten-1-yl benzoate instead of 3-buten-1-ol. No significant improvement is, however, observed, the final molecular weight being 5500 after 24 h.

Data of ATRA mediated by the same catalyst although at a lower temperature (60 °C) are listed in Table 2. It must be noted that molecular weights have been measured by SEC and are thus apparent values. When 3-buten-1-yl benzoate is grafted, the apparent molecular weight remains unchanged for at least 24 h. The situation changes in the case of ATRA of 3-buten-1-ol because then the apparent molecular weight (20,000) decreases beyond 8 h of reaction consistent with chain degradation promoted by hydroxyl groups. It thus appears that temperature is a key parameter and that 60 °C is a good compromise between fast reaction and minimized degradation. Moreover, hydroxyl groups do not have to be protected if a reaction yield higher than 40% is not required.

3.2. Grafting of PCL by unsaturated carboxylic acids

ATRA of vinylacetic acid onto poly(αClεCL-*co*-εCL) has been repeated under the same conditions as for the grafting of 3-buten-1-ol (CuBr/Me_6-Tren, DMF, 60 °C, four equivalents of vinyl acetic acid). However, the ^{1}H NMR spectrum for the copolymer does not confirm the addition of vinylacetic acid (not shown), although the content of α-chlorinated units has decreased from 50 to 26%. The

Table 2
Time dependence of the grafting of 3-buten-1-ol at 60 °C

Olefin	3-Buten-1-yl benzoate			3-Buten-1-ol		
Time (h)	Mn(SEC)	M_w/M_n	Pendant chloride conversion (%)	Mn(SEC)	M_w/M_n	Pendant chloride conversion (%)
1	11,000	1.45	11	20,000	1.55	16
4	12,000	1.40	26	21,000	1.60	28
8	12,000	1.40	31	20,000	1.55	37
24	12,000	1.40	51	10,000	1.80	52

explanation is that poly(αClεCL) is reduced to poly(εCL) by the CuBr/Me_6-Tren catalyst in the presence of carboxylic acid. For the sake of comparison, poly(αClεCL-*co*-εCL) has been reacted with acetic acid in the presence of CuBr/Me_6-Tren in DMF for 3 h with acetic acid. A sharp decrease in the content of αClεCL from 49 mol% down to 25 mol% is expectedly observed. As a rule, CuBr/Me_6-Tren/DMF is not tolerant of carboxylic acid. Although out of the scope of this paper, this reaction could be useful to get rid of the halogen end-group of polymers prepared by ATRP, if needed.

HMTETA has been used instead of Me_6-Tren in order to decrease the extent of the undesired reduction reaction. Indeed, the αClεCL content of poly(αClεCL-*co*-εCL) remains constant after reaction with CuBr/HMTETA/acetic acid in DMF at 60 °C for 3 h. The remarkable tolerance of CuBr/HMTETA of carboxylic acid allows for the grafting of vinyl acetic acid onto poly(αClεCL-*co*-εCL) as shown by Fig. 3. The extent of the olefin addition has been calculated by ^{1}H NMR spectroscopy (Fig. 4) according the Eqs. (3)–(5). No detrimental reduction of α-chlorinated-ε-caprolactone has been observed.

$$F_{\mathrm{ATRA}} = \frac{I_B/5}{I_B/15 + I_A/6 + I_{C,D,E,F}/3} \quad (4)$$

$$F_{\alpha\mathrm{Cl}\varepsilon\mathrm{CL}} = \frac{(I_{C,D,E,F} - 2/5I_B - I_A)/3}{I_B/15 + I_A/6 + I_{C,D,E,F}/3} \quad (5)$$

3.3. Grafting of epoxides onto PCL

ATRA of 1,2-epoxyhex-5-ene onto poly(αClεCL-*co*-εCL) has also been investigated in DMF at 60 °C, by using both the HMTETA and Me_6-Tren ligands. Whenever CuBr/Me_6-Tren is the catalyst, a reaction takes place, that makes the copolymer insoluble and thus not suited to characterization by ^{1}H NMR and SEC. However, this problem is no longer faced when ATRA is mediated by CuBr/HMTETA. The pendant chloride conversion is 42% after 8 h without any significant degradation of the polyester chains. Fig. 5 shows the ^{1}H NMR spectrum for the modified copolymer, the reaction progress being calculated with Eqs. (3), (6) and (7).

$$F_{\mathrm{ATRA}} = \frac{I_B}{I_B/3 + I_A/6 + I_{C,D,E,F}/3} \quad (6)$$

$$F_{\alpha\mathrm{Cl}\varepsilon\mathrm{CL}} = \frac{(I_{C,D,E,F} - 2I_B - I_A)/3}{I_B/3 + I_A/6 + I_{C,D,E,F}/3} \quad (7)$$

3.4. Thermal properties

The poly(αClεCL-*co*-εCL) copolymers added by ATRA with (at least 30 mol%) the olefins under consideration in this work are amorphous and their T_g is reported in Table 3. Fig. 6 compares the TGA profiles for poly(αClεCL-*co*-εCL)

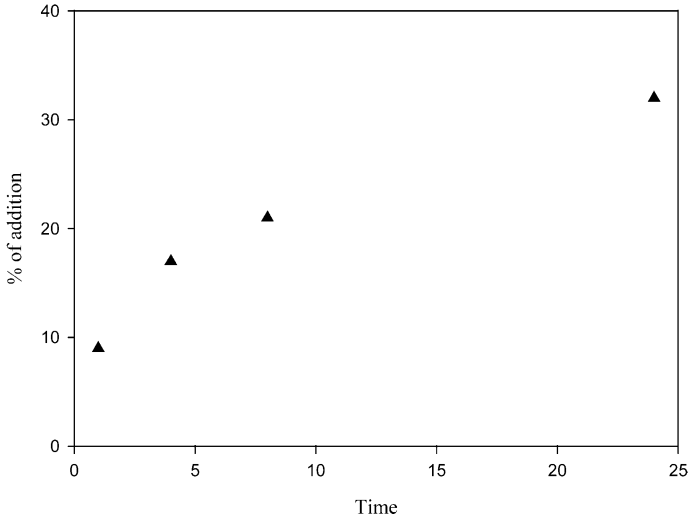

Fig. 3. Time dependence of the ATRA of vinylacetic acid onto poly(αClεCL-*co*-εCL) in the presence of CuBr/HMTETA, in DMF, at 60 °C.

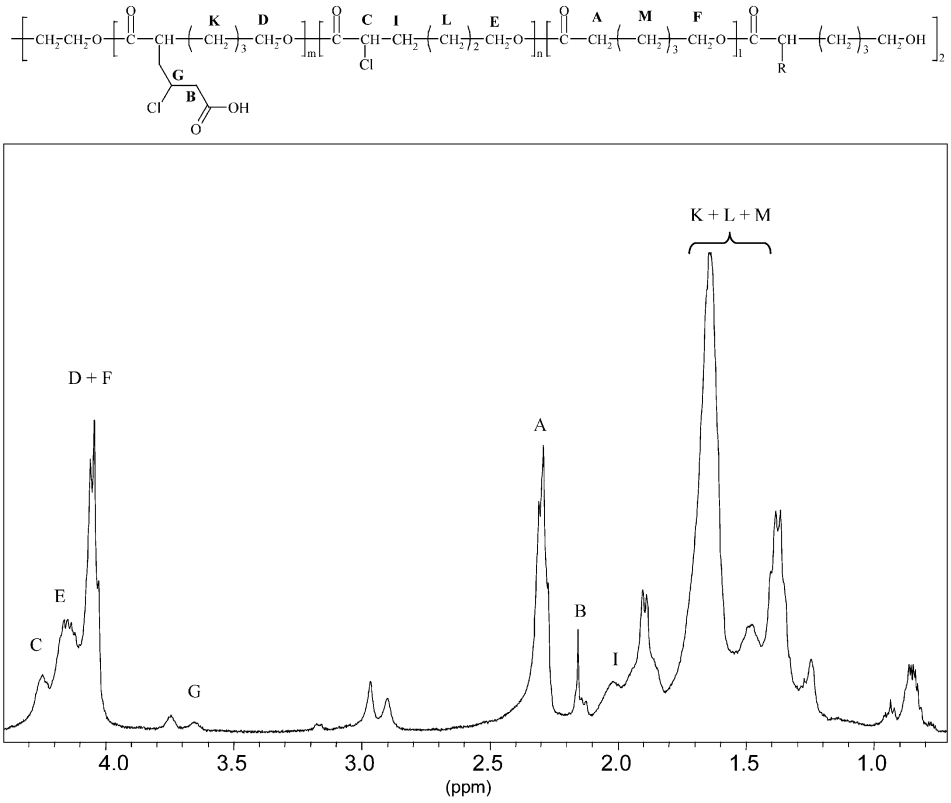

Fig. 4. ^{1}H NMR spectrum of poly(αClεCL-*co*-εCL) after the CuBr/HMTETA-mediated ATRA of vinylacetic acid.

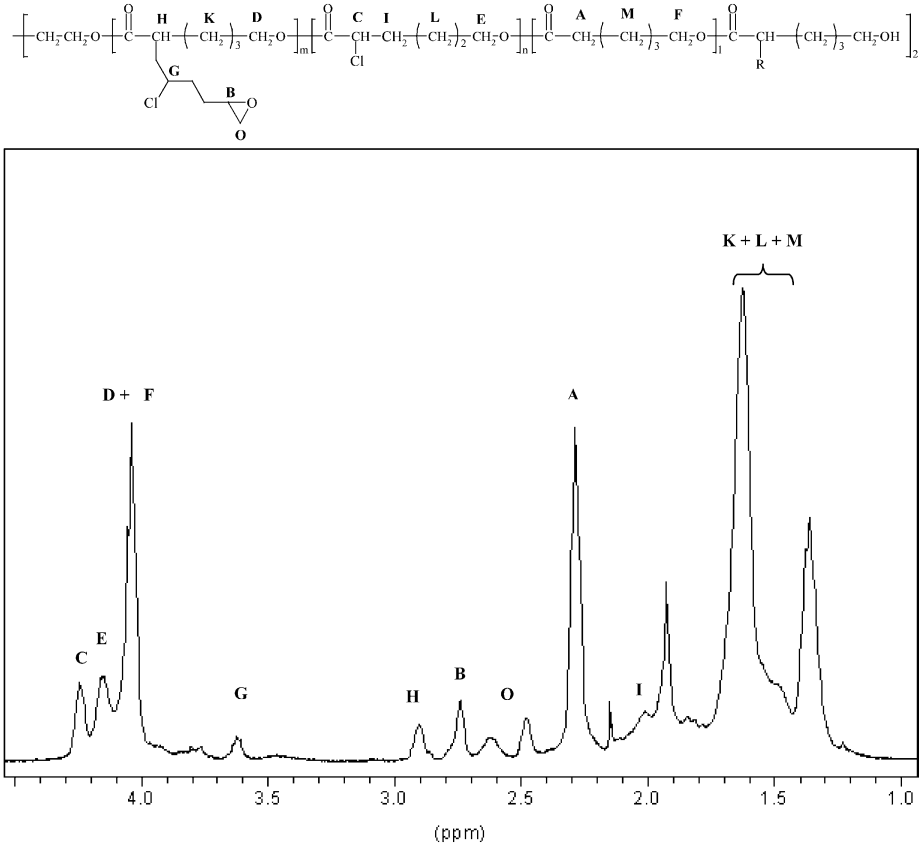

Fig. 5. ^{1}H NMMR spectrum for the poly(αClεCL-*co*-εCL) copolymer after the CuBr/HMTETA-mediated ATRA of 1,2-epoxyhex-5-ene.

Table 3
DSC analyses of poly(αClεCL-*co*-εCL) and copolymers added with functional olefins

Copolymer	F_{ATRA}	T_g (°C)	T_m (°C)
Poly(αClεCL-*co*-εCL)	0.49	−56	–
After ATRA of 3-buten-1-ol	0.37	−54	–
After ATRA of vinylacetic acid	0.32	−48	–
After ATRA of 2-epoxyhex-5-ene	0.42	−42	–

before (a) and after ATRA of 3-buten-1-ol (b), vinyl acetic acid (c) and 1,2-epoxyhex-5-ene (d) onto poly(αClεCL-*co*-εCL). Copolymers grafted by ATRA degrades faster than their poly(αClεCL-*co*-εCL) precursor, at a rate that depends on the grafted olefin as follows: 3-buten-1-ol < vinyl acetic acid < 1,2-epoxyhex-5-ene. The degradation profile turns also more complex, particularly when 1,2-epoxyhex-5-ene has been grafted (Fig. 6.; curve d), which is indicative of a modified degradation mechanism.

4. Conclusions

α-Chloro-ε-caprolactone is easily prepared by the Baeyer–Villiger oxidation of 2-chlorocyclohexanone and copolymerized with ε-caprolactone with a Sn(IV) alkoxide initiator. These statistical copolymers are ideal precursors for the synthesis of poly(ε-caprolactone) bearing either hydroxyl or carboxyl acid or epoxy groups randomly distributed along the chains. Indeed, the pendant activated chlorides of the copolymers are prone to react by ATRA with olefins. ATRA of 3-buten-1-ol is highly efficient when mediated by the CuBr/Me_6-Tren catalyst at 60 °C. More than 95% of the chloride units of a copolymer with an equimolar composition have reacted within 4 h provided that a four-fold molar excess of the olefin was used. No significant degradation of the polyester chains is observed. A remarkable solvent effect has been reported because the ATRA reaction does not take place anymore when toluene is substituted for DMF. ATRA of an olefin containing either a carboxylic acid or an epoxide is out of control when mediated by the CuBr/Me_6-Tren catalyst. Indeed, the chloride units of the poly(αClεCL-*co*-εCL) copolymer are reduced whenever vinyl acetic acid is the olefin. In case of 1,2-epoxyhex-5-ene, the copolymer becomes rapidly insoluble. These problems have been solved by using HMTETA rather than Me_6-Tren as ligand for CuBr. The control is, however, restored at the expense of the reaction yield. Interestingly enough, reduction of α-chlorinated esters by a carboxylic acid (e.g. acetic acid) in the presence of CuBr/Me_6-Tren is a possible way to eliminate the chloride end-group of polymers prepared by ATRP. The ATRA strategy reported in this work could be extended to oligomers end-capped by a double bond, e.g. α-unsaturated, ω-hydroxy poly(ethylene oxide), with the purpose to prepare amphiphilic graft copolymers. The ω-hydroxy group does not require to be protected during ATRA and remains available for further grafting and macromolecular engineering. This extension is under current investigation.

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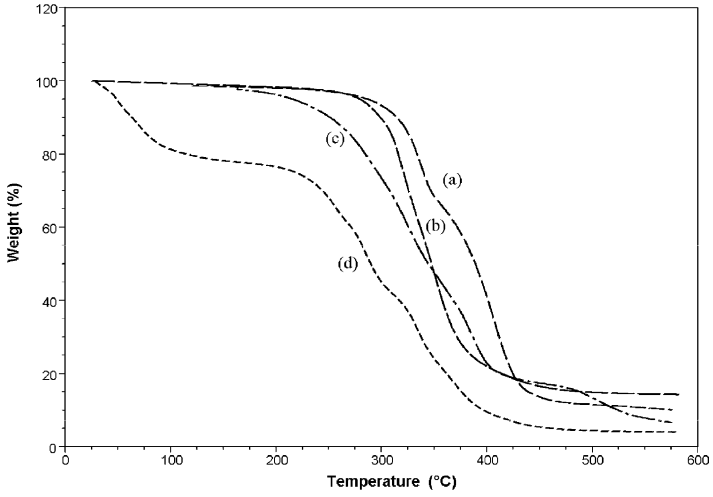

Fig. 6. TGA curves for poly(αClεCL-*co*-εCL) before (a) and after ATRA of vinyl acetic acid (F_{ATRA} = 0.32); (b), 3-buten-1-ol (F_{ATRA} = 0.37) (c) and 1,2-epoxyhex-5-ene (F_{ATRA} = 0.42) (d).

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