Kinetic Study of the Al-Schiff's Base Initiated Polymerization of ε-caprolactone and Synthesis of Graft Poly(methylmethacrylate-g-caprolactone)

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Summary: Graft copolymers of polycaprolactone (PCL) on polymethacrylate (PMMA) backbone have been successfully synthesized and characterized by SEC, ^{1}H and ^{13}C NMR spectroscopy. The strategy used consisted of polymerizing ε-CL, followed by end-functionalization of the resulting PCL using methacryloyl chloride. Free radical polymerization of the methacryl double bond lead to the C-C polymer backbone and an overall graft copolymer. The polymerization of ε-caprolactone was achieved using Al-Schiff's base isopropoxide (HAPENAlO^{i}Pr) in DCM at ambient temperature. SEC and MALDI analysis of the polymers confirmed that mostly linear chains were obtained with the Al initiator, up until high monomer conversion. The low molar mass PCL was then end-capped with a methacryloyl group, in a quantitative manner, as evidenced by ^{1}H NMR. The macromonomer thus obtained was copolymerized in small proportions with methyl methacrylate by conventional free radical polymerization and atom transfer radical polymerization (ATRP). Analysis of the products by NMR and SEC showed the presence of true graft copolymers and the absence of homopolymers.

Keywords: graft copolymer; polycaprolactone; polymethylmethacrylate

Introduction

Graft copolymers are interesting materials as they can be tailored in such a way as to combine unique properties of two different homopolymers. In this article, the focus shall be on the grafting of polyester chains such as polycaprolactone (PCL) onto polymethacrylate (PMMA) backbone. The latter is a stiff non-degradable hydrophobic polymer which finds wide use in the biomedical field (dental prostheses, bone cement, artificial eye lenses, pacemakers) while PCL is a more flexible bioresorbable polyester. It is often used as a matrix for long-term drug delivery due to its low biodegradability. Graft copolymers of PCL onto methacrylate backbone have been synthesized by various groups via the PCL-macromonomer route. Dubois *et al.*[1–4] have end-functionalized PCL and have synthesized PCL graft copolymers with various hydrophilic methacrylate polymers such as polyhydroxyethyl methacrylate (PHEMA) and polyN,N-dimethylamino-2-ethyl methacrylate (PDMAEMA). The combination of the two polymers lead to control on the hydrophobic/hydrophilic balance and gave rise to amphiphilic behavior. Graft copolymers of PCL onto polydimethacrylamide (PDMA), polymethyl methacrylate (PMMA) and copolymers of poly(DMA-co-MMA) have also been synthesized [5]. Such grafts have been proposed as drug delivery matrices, since varying the ratio of the components tailors the swelling behaviour and hence biodegradation rate of the polyester moieties. Other methods, such as the grafting-from technique, have also been successfully used to access p(HEMA-g-CL). It requires the preliminary synthesis of copolymers containing initiator sites, such as hydroxyl groups, for the grafting of PCL chains [6,7].

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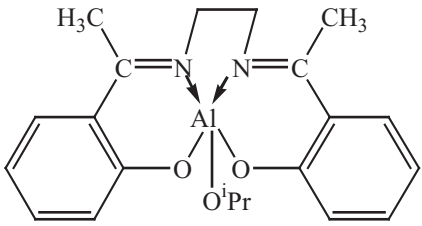


Figure 1.
Structure of HAPENAlO^{i}Pr (**I**).

The synthesis of the graft copolymers via the use of PCL-macromonomers is an interesting pathway to well-defined copolymers. In a first step, low molar mass polycaprolactone is synthesized either by the ROP of ε-caprolactone (ε-CL) using aluminium alkoxide as initiator Al(O^{i}Pr)$_3$[8,9] or by direct polycondensation without use of catalyst [5]. The PCL-macromonomer is then obtained by either end-functionalizing the hydroxy-PCL chain with a methacryloyl group or by polymerizing ε-CL using an initiator bearing a carbon-carbon double bond, e.g., diethylaluminium 2-hydroxyethyl methacrylate ($Et_2AlO(CH_2)_2$-$COC(CH_3)=CH_2$) [2].

Herein, we report on the synthesis of PMMA-g-PCL copolymers via a macromonomer pathway. The synthesis of PCL was carried out using our previously reported Al-Schiff's base complex [10–12], namely HAPENAlO^{i}Pr (I) (Figure 1) as initiator.

The synthesis of the PCL-macromonomer was achieved by end-functionalizing the hydroxy-terminated PCL chains after hydrolysis with methacryloyl chloride (Scheme 1). The macromonomer, ω-methacryl-polycaprolactone (ω-MPCL), was copolymerized both by conventional free radical polymerization and by Atom Transfer Radical Polymerization (ATRP) leading to graft copolymers.

Polymerization of ε-caprolactone (ε-CL)

Kinetic Study

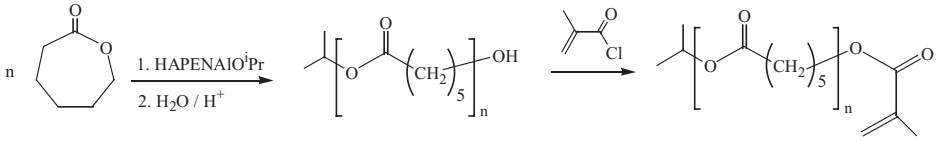
The polymerization of ε-CL was carried out under argon at 25 °C using initiators **I** (HAPENAlO^{i}Pr) and **II** (AlO^{i}Pr$_3$), in DCM and toluene, according to the respective solubility of the initiators. The kinetics of the polymerization at [M]/[I] = 10 was investigated first. A linear variation of $\ln[M]_o/[M]_t$ vs time was obtained using **I** in DCM and **II** in toluene for ε-CL polymerization. This is an indication of the "living" character of the polymerization (Figure 2).

Polymerization using Al(O^{i}Pr)$_3$ (**II**) in DCM gives rise to a curve plot of $\ln[M_o]/[M_t]$ vs time indicating the presence of transfer reactions. DCM being more polar than toluene, prevents the formation of aggregates of **II** whose size control the activity of the initiator, as previously reported by Ropson *et al.*[13]. The kinetics of the polymerization of ε-CL was further investigated at lower initiator concentrations. Figure 3 shows the plots obtained when polymerizations are initiated by **I** and **II** at 25 °C using [M]/[I] 50 and 100.

The linear plots confirm the stability of the active centers at low initiator concentrations. The apparent rate constants of the polymerization (k_{app}) values for the two initiators listed in Table 1 show a faster polymerization of ε-CL with Al(O^{i}Pr)$_3$ as compared to the Al-Schiff's base complex.

Presence of Linear v/s Cyclic Species

The polymerizations of ε-CL using HAPENAlO^{i}Pr (**I**) and Al(O^{i}Pr)$_3$ (**II**) were followed both by ^{1}H NMR and SEC. Molar mass of the crude polycaprolactone, i.e.



Scheme 1.
Synthesis of PCL-macromonomer.

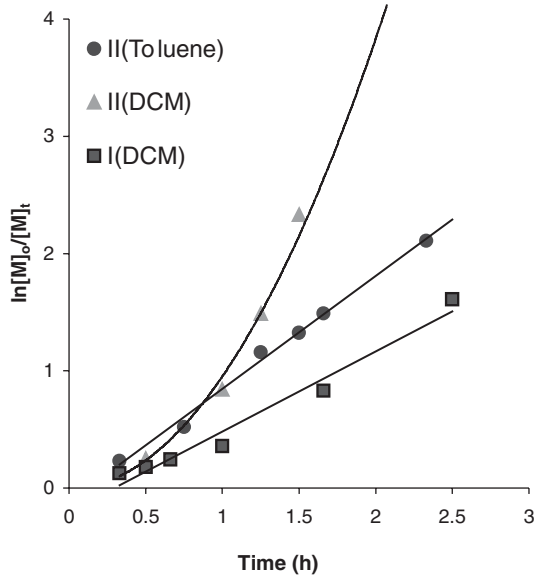


Figure 2.
Semi-logarithmic plots of conversion against time for the polymerizations carried out in toluene (initiator **I**) and DCM (initiator **II**) at 25 °C, [M = 1M, [M]/[I] = 10.

before precipitation, was determined by ^{1}H NMR using end group analysis [12]. The results are summarized in Table 2.

An increase in the polydispersity index (M_w/M_n) with conversion is observed using **I** at [M]/[I] = 10. This indicates the probable

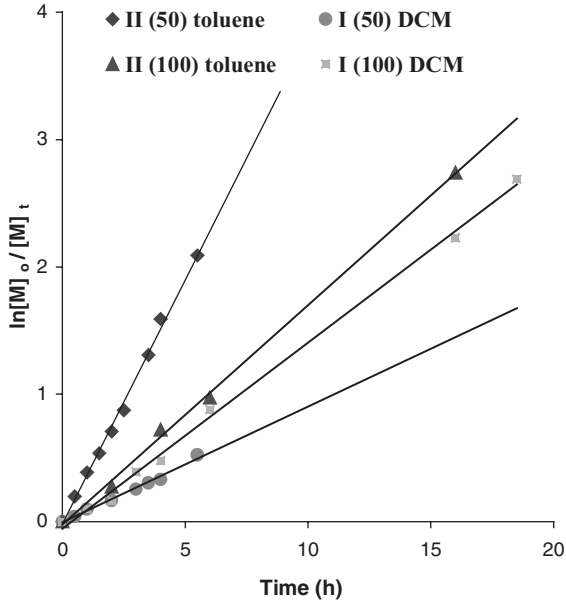


Figure 3.
Semi-logarithmic plots of conversion against time for the polymerizations in toluene and DCM at 25 °C initiated by **I** and **II**, [M] = 1 M and [M]/[I] = 50 and 100.

Table 1.
Apparent rate constants of polymerization at 25 °C, [M] = 1 M and [M]/[I] = 10, 50 and 100.

Initiator (solvent)	$k_{app} \times 10^3$ (h^{-1})		
	[M]/[I] = 10	[M]/[I] = 50	[M]/[I] = 100
I (DCM)	683	294	144
II (Toluene)	963	378	170

occurrence of side reactions, such as inter/intra transesterifications, at high conversion. There is a good correlation between calculated and experimentally determined molar masses (^{1}H NMR) for initiator **I** up to high conversion. However, for initiator **II**, this correlation is not good and moreover, a decrease in experimental molar mass is also observed at higher monomer conversion (Figure 4). This is an indication of the occurrence of intermolecular side reactions [14,15].

The occurrence of side reactions leading to cyclic species was further investigated. Both crude polymer samples and methanol-precipitated polymers were subjected to MALDI-TOF-MS analysis. The spectrum of crude polymer **PCL4**, obtained with HAPENAlO^{i}Pr, (Figure 5) shows the presence of linear chains with ester end group (–COO^{i}Pr) mainly together with a small percentage of cyclic species. The presence of the latter suggests that intramolecular transesterification reactions are also taking place to some extent. This has also been observed for DL-lactide polymerization especially at relatively high conversions [15].

Occurrence of side reactions was also studied by ^{13}C NMR with focus on the carbonyl region. The crude PCL obtained using **I** and **II** as initiators, at [M] = 1 M and [M]/[I] = 10, 50 and 100 were characterized by ^{13}C NMR. When **I** is used for polymerization at [M]/[I] = 10, at 85% conversion, expansion of the carbonyl region of the spectrum showed the presence of three signals at 173.1, 173.6 and 173.8 ppm (Figure 6 (**A**)). The more intense signal **a** at 173.6 ppm corresponds to the carbonyl in the main polymer chain and that at 173.8 ppm (**c**) to the CO in the ultimate caprolactone group. The signal **b** at 173.1 ppm is assigned to the end chain isopropoxy carboxylate group, thereby supporting the coordination-insertion mechanism of the polymerization. At 100% conversion, analysis of the polymer by ^{13}C NMR shows the presence of an additional peak **d** at 173.4 ppm, which is probably due to the occurrence of cyclic chains from transesterification reactions (Figure 6 (**B**)). Analysis of PCL previously precipitated in methanol showed no such signal, indicating that cyclic species are eliminated upon precipitation. The signal at 173.4 ppm is also not observed when polycaprolactone is obtained using Al(O^{i}Pr)$_3$ as initiator, thus indicating that only intermolecular side reactions occur.

Table 2.
Polymerization of ε-caprolactone using HAPENAlO^{i}Pr (**I**) and Al(O^{i}Pr)$_3$ (**II**) at 25 °C.

Ref.	Initiator (Solvent)	[M]/[I]	Time (h)	Conv. (%)[a]	M_n calc[b]	M_n ^{1}H NMR	M_n SEC[c]	M_w/M_n
PCL1	**I** (DCM)	10	1	30.0	340	370	1270	1.3
PCL2			1.66	56.5	640	750	1850	1.3
PCL3			2.5	80.0	910	970	2220	1.4
PCL4			3.5	100	1140	1370	4430	1.6
PCL5		50	7.5	100	5700	5400	7900	1.6
PCL6		100	21	100	11400	10800	9500	1.7
PCL7	**II** (toluene)	10	1	51.3	580	680	—	—
PCL8			1.5	73.4	840	2100	—	—
PCL9			2.33	87.9	1000	1800	—	—
PCL10			2.83	93.4	1060	1480		
PCL11			3	100	1140	1250	4000	1.7
PCL12		50	5.5	100	5700	6500	—	1.5

[a] determined from ^{1}H NMR.
[b] $M_n^{calc} = 114 \times [M]/[I] \times (conversion/100)$.
[c] M_n^{SEC} calculated w.r.t polystyrene standards using crude polymer samples.

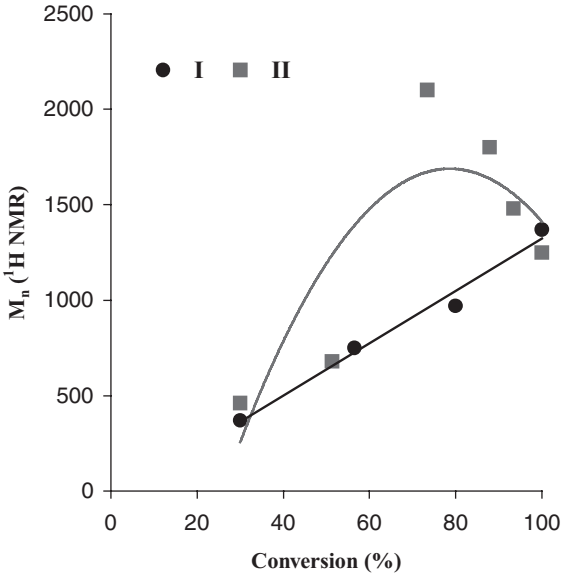


Figure 4.
Plots of molar masses (^{1}H NMR) of PCL obtained using **I** (DCM) and **II** (toluene) vs monomer conversion.

This result is in agreement with previous results obtained by SEC and NMR. Only one C=O is obtained at [M]/[I] = 50 and 100 using both initiators due to the higher molar mass of the polymer.

Synthesis of Macromonomer: ω-methacryl Polycaprolactone (ω-MPCL)

End-functionalization of PCL Chains with Methacryloyl Chloride

Low molar mass polycaprolactone was prepared using HAPENAlO^{i}Pr (**I**) and Al(O^{i}Pr)$_3$ (**II**) as initiators ([M]/[I] = 10). The polymers were then treated with acidified methanol to cleave the Al-oxygen bond, thus giving hydroxy-terminated polycaprolactone (PCL-OH) chains. The latter were reacted with a five-fold excess methacryloyl chloride and the crude product was precipitated in methanol to yield ω-methacryl-polycaprolactone (ω-MPCL). The hydroxy-terminated PCL and the corresponding macromonomers were characterized by ^{1}H and ^{13}C NMR and by SEC (Table 3). Low molar mass polycaprolactone and cyclics are lost upon precipitation, hence bringing about a decrease in the polydispersity indices.

The end-functionalized PCL were analysed by ^{1}H NMR (Figure 7) and the degree of end-capping by the methacryloyl group was determined. For that purpose, the intensities of the signals of protons of the methacryloyl group (H^a, H^b) at 5.50 and 6.03 ppm were compared to that of the methine proton (H^c) at 4.91–5.07 ppm and a high degree of end-capping was thus confirmed. The spectra also showed that the signal of the α-hydroxymethylene (–CH$_2$OH) at 3.63–3.67 ppm has completely disappeared in favor of a new signal at 4.06–4.11 ppm (H^d).

^{13}C NMR of the functionalized PCL showed peaks at 125.3 and 136.5 ppm corresponding to the C=C of the methacryloyl unit. In addition, the signal at 173.8 ppm corresponding to the C=O in the ultimate group of PCL disappeared and a new signal at 167.5 ppm was obtained. The latter was assigned to the carbonyl of the methacryloyl unit.

M_{peak}	Assignment
1970	Cyclic $[O(CH_2)_5CO]_{17}$
2030	H-$[O(CH_2)_5CO]_{17}O^iPr....K^+$
2084	Cyclic $[O(CH_2)_5CO]_{18}$
2145	H-$[O(CH_2)_5CO]_{18}O^iPr....K^+$

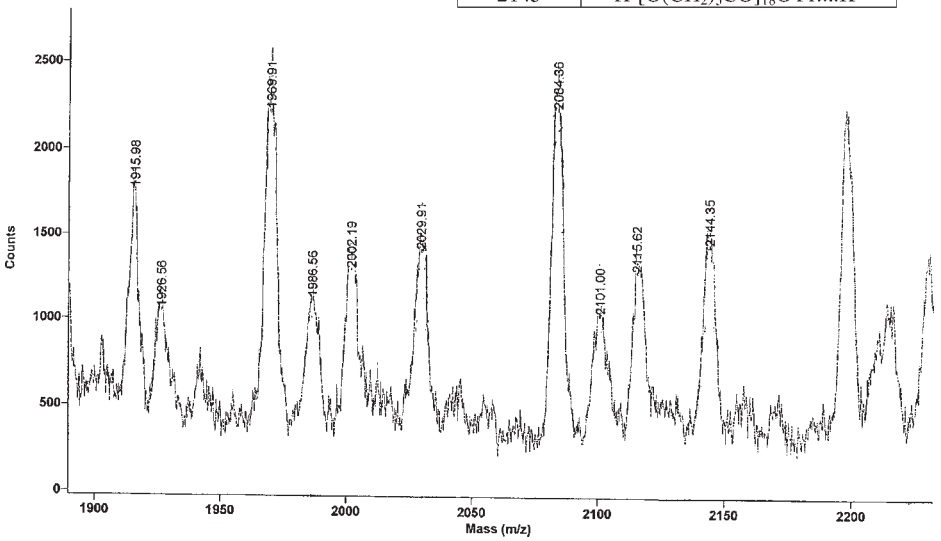


Figure 5.
MALDI spectrum of PCL4.

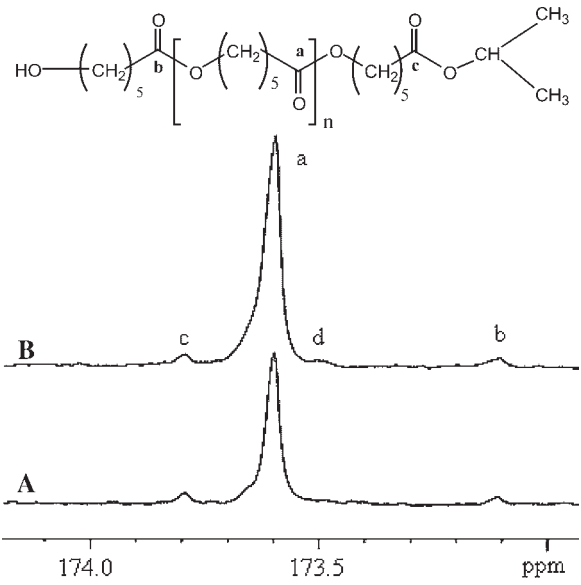


Figure 6.
Carbonyl region of the ^{13}C NMR spectrum of polycaprolactone ([M]/[I] = 10) initiated by HAPENAl(O^iPr) at (A) 85% conversion and (B) 100% conversion.

Table 3.
Characterization of crude PCL-OH and ω-MPCL using initiators **I** and **II** at 25 °C, [M] = 1 M, [M]/[I] = 10, conversion 100%.

Ref.	Initiator	M_n calc[a]	M_n ^{1}H NMR	M_n ^{1}H SEC[b]	PDI
PCL4	**I**		1370	4430	1.6
ω-PCL4			2740	4600	1.36
PCL11	**II**	1140	1250	3800	1.7
ω-PCL11			1710	4000	1.4

[a] $M_n$calc = [M]/[I] × 114.
[b] Using polystyrene standards.

Copolymerization of Macromonomer with Methyl Methacrylate

ω-MPCL4 (M_n (^{1}H NMR) = 2700, DP_n = 23) was copolymerized with methyl methacrylate (MMA). Copolymerization was carried out in toluene at 70 °C for 15 hours using (i) AIBN as a free radical initiator and (ii) EBBr/CuBr/bpy as ATRP initiator/catalyst system (Scheme 2). Graft copolymers of various compositions were synthesized by mixing the required amount of the two comonomers, ω-MPCL and MMA. The concentration of ω-MPCL in the comonomer feed varied between 1–5 mol%.

The polymer solutions were precipitated in methanol, and the filtrates were dried under vacuum. The yield varied between 80–85%. The graft copolymers were characterized by ^{1}H and ^{13}C NMR and by SEC. The results of the copolymerization by both systems are summarized in Table 4.

The graft copolymers synthesized by free radical polymerization were partially soluble in most organic solvents. However, they swelled in toluene and chloroform. The ^{1}H and ^{13}C NMR analyses were carried out in these solvents but no SEC characterization was performed due to the low solubility. On the other hand, the polymers obtained by ATRP were soluble in most organic solvents.

A comparison of the SEC chromatograms before and after grafting (Figure 8) indicates that ω-MPCL and MMA have successfully copolymerized. A higher concentration of PCL chains lead to copolymers with broader molar mass distributions (Table 4, Copolys 4 and 5). One possible explanation is that PCL is not easily incorporated in the glassy PMMA matrix. Indeed, blends of PCL and PMMA have

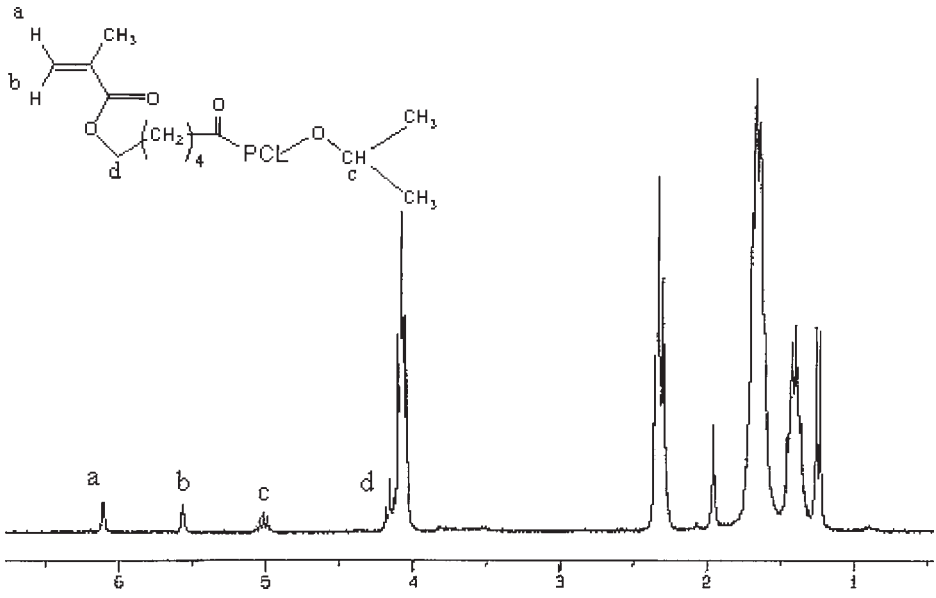
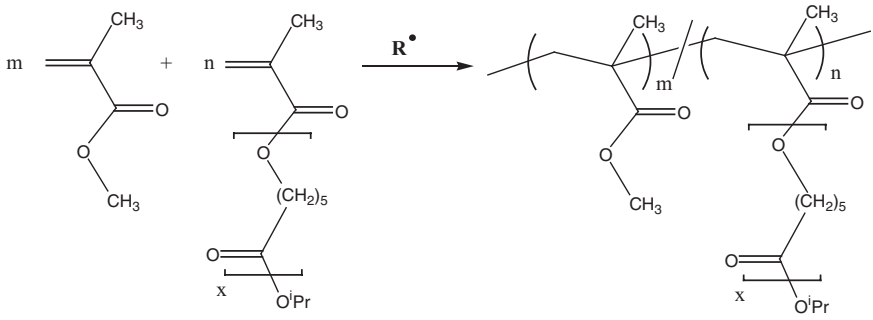


Figure 7.
^{1}H NMR of ω-MPCL in $CDCl_3$.



Scheme 2.
Copolymerization of MMA and ω-MPCL by free-radical polymerization and ATRP (R= radical initiator).

shown that there is no compatibility of the two polymers, resulting in phase segregation of PCL in the PMMA matrix [16].

Investigation of the chemical structures of the copolymers, after precipitation in methanol, by ^{1}H (Figure 9) and ^{13}C NMR confirmed the presence of both comonomers. The signals appearing in the carbonyl region of the ^{13}C NMR at 173.6 ppm (C=O polycaprolactone) and 177.2–178.6 ppm (C=O polymethacrylate) showed the presence of both comonomeric units in the copolymers.

The copolymer compositions were determined by ^{1}H NMR by using the relative intensities of the signals of the methylene protons of PCL at 4.0–4.1 ppm and the methyl protons of PMMA at 3.5–3.7 ppm. The concentration of PCL in the copolymer is slightly lower than expected (Table 4). This can be due to the loss of unpolymerized ω-MPCL upon precipitation. Another possible reason is the masking of some PCL chains in the graft copolymer by the PMMA C–C backbone [17]. Indeed, when low concentrations of PCL are added to the PMMA (Copolys 3 and 4), the isopropoxy end-group (4.9–5.0 ppm) is not visible in the ^{1}H NMR. This signal can only be observed in the ^{1}H NMR spectrum of Copoly 5.

Conclusion

The use of Al-Schiff's base complex enabled the controlled polymerization of ε-CL. The end-functionalization of polycaprolactone-OH chains into methacryl-PCL was successfully achieved. Subsequent polymerization with MMA by ATRP yielded graft copolymers with a vinyl backbone and side PCL chains present in a level up to a maximum of 4.3 mol % as evidenced by ^{1}H NMR. A thorough thermal characterization of the PMMA-g-PCL graft copolymers is underway. Their use as scaffolds for bone regeneration is also being investigated.

Table 4.
Copolymerization of MMA with ω-MPCL ($[M_{total}]_0 = 2$ M).

Copolymer	Initiator	f $_\omega$-MPCL[a] (mol -%)	F $_\omega$-MPCL[b] (mol -%)	M_n^{SECc}	M_w/M_n
Copoly 1	AIBN	1	0.4	—	—
Copoly 2		2	1.4	—	—
Copoly 3	EBBr/CuBr/bpy	1	0.5	12000	1.31
Copoly 4		2	1.6	13800	1.53
Copoly 5		5	4.3	8500	1.65

[a] Initial concentration of ω-MPCL in co-monomer feed.
[b] Concentration of PCL in copolymer feed, as determined by ^{1}H NMR spectroscopy.
[c] Determined by SEC in THF, using polystyrene standards.

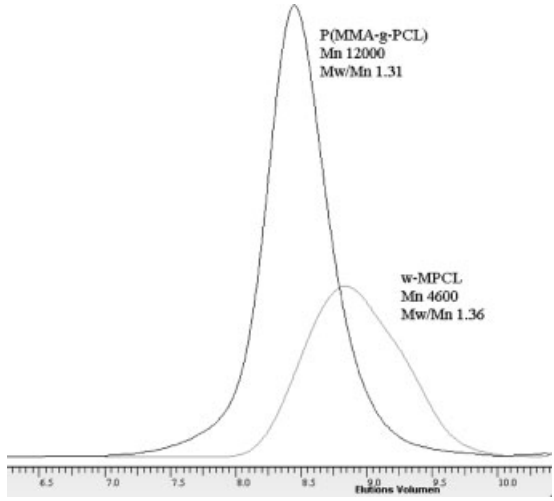


Figure 8.
SEC curves of ω-MPCL and graft copolymer, Copoly 3 in THF as eluent.

Experimental

Materials

Monomer – ε-Caprolactone and methyl methacrylate were used as received from Aldrich. Methacryloyl chloride was synthesized by reacting an excess of thionyl chloride with methacrylic acid in the presence of 4-methoxyphenol (1 %) to inhibit the polymerization of the double bond. The reaction mixture was stirred at 80 °C for 4 hours and methacryloyl chloride was distilled off at 95–97°C. It was characterized by ^{1}H and ^{13}C NMR in $CDCl_3$.

^{1}H NMR ($CDCl_3$): CH_3 (3H, 1.94 ppm), vinylic CH_2 (1H, 1H, 5.96 and 6.42 ppm).

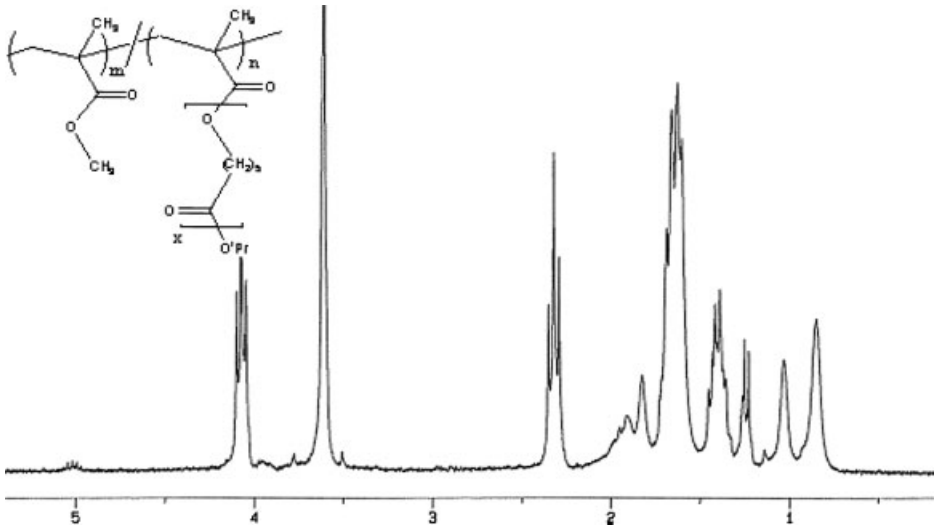


Figure 9.
^{1}H NMR of graft copolymer, Copoly 5, in $CDCl_3$.

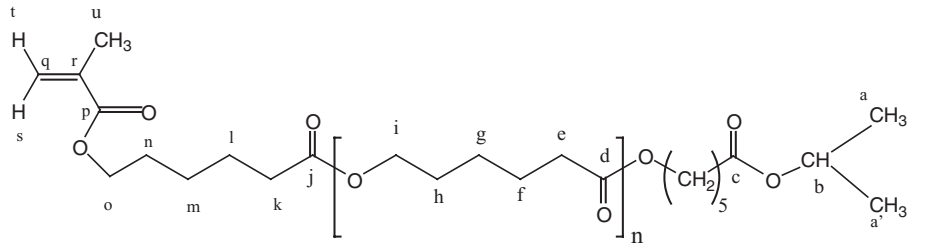


Figure 10.
ω-methacryl-polycaprolactone.

^{13}C NMR ($CDCl_3$): CH_3 (18.6 ppm), $\underline{C}H_2$–$C(CH_3)$ (133.5 ppm), $\underline{C}(CH_3)$–CH_2 (140.8 ppm), CO (168.8 ppm).

Solvent – Toluene was first refluxed and then distilled over sodium under nitrogen and kept under argon. Dichloromethane was refluxed, then distilled over CaH_2 and kept under argon. Methanol was purified according to Lund and Bjerrum method.

Initiator – $Al(O^iPr)_3$ was used as obtained from Riedel-de-Haën. HAPE-NAlO^{i}Pr was synthesized as described previously [12,18].

Instruments

^1H and ^{13}C NMR spectra were recorded in 5 mm sample tubes in $CDCl_3$ using an FT Bruker 250 MHz spectrometer at 25 °C. All ^{13}C NMR spectra were recorded using a similar set of parameters (number of scans: 12 000, acquisition time: 2.37 s.)

MALDI-TOF-MS was performed using a Perseptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm-3 ns pulse), a delayed extraction and a reflector. It was operated at an accelerating potential of 20kV in linear mode. The MALDI mass spectra represent averages over 256 consecutive laser shots (3 Hz repetition rate). The polymer solutions (2–5 gL^{-1}) were prepared in THF. The matrix, 1,8-dihydroxy-9[10H]-anthracenone (dithranol), was also dissolved in THF (25 gL^{-1}). A 10 μL portion of the polymer solution was mixed with 20 μL of the matrix solution. A sodium iodide solution (10 μL of a solution of 20 gL^{-1} in THF) was finally added to favor ionization by cation attachment. 1 μL of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Standards (polystyrenes of known structure, $M_n = 3420$ and 7600 $gmol^{-1}$ purchased from Polymer Standards Service) were used to calibrate the mass scale using the two point calibration software 3.07.1 from PerSeptive Biosystems. In all cases, to determine m/z, mass of the sodium cation was added.

SEC measurements were carried out using a PSS equipment (SDV LinearXL column), using THF as eluant at a flow rate of 1 ml/min and an RI detector. Calibration was effected with polystyrene standards.

Polymerization of ε-caprolactone

All polymerizations were conducted under argon in glass tubes. The monomer was first dissolved in the solvent at ambient temperature followed by addition of the initiator. After the desired time of polymerization, samples of the crude product were analysed by ^1H NMR to determine the percentage conversion and by SEC. The reaction was stopped by precipitating the polymer solution in acidified methanol. The polymer was filtered and finally dried under vacuum at 40°C.

Encapping of Polycaprolactone - Synthesis of ω-methacryl-polycaprolactone

Polycaprolactone (1.14 g, 0.01 mol) and 4-methoxyphenol (62 mg, 0.05 mmol) were heated, with stirring, to 50–60°C in a boiling tube in an oil bath. Methacryloyl chloride (0.52 g, 5 mmol) was added to the molten polymer and the mixture was well stirred

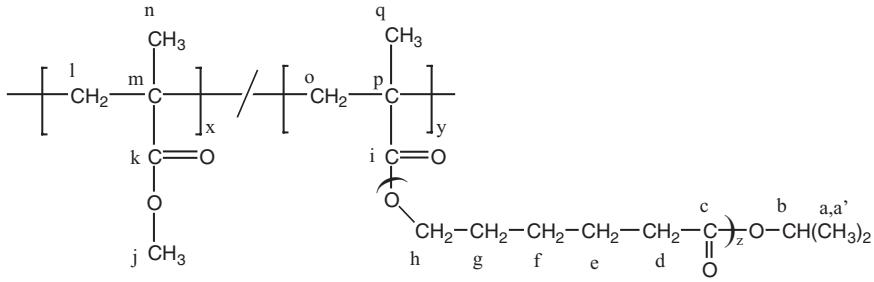


Figure 11.
Poly(methacryl-g-caprolactone).

under nitrogen. The reaction was carried out at 90 °C for 10 hrs under a constant nitrogen flux. The reaction vessel was cooled and the resulting pale brown solid was well washed thrice with cold methanol (3 × 10 mL) to remove excess methacryloyl chloride and the inhibitor. The white precipitate was then filtered and dried under vacuum at room temperature and characterized by ^{1}H and ^{13}C NMR (Figure 10) and SEC. Yield = 0.782 g, 70%.

^{1}H NMR (CDCl$_3$): δ (ppm) = 1.16–1.18 (d, 2C$\underline{H}_3^{a,\,a'}$), 1.26–1.38 (m, C$\underline{H}_2^{g}$), 1.50–1.65 (t, 2C$\underline{H}_2^{f,\,h}$), 1.88 (s, C$\underline{H}_3^{u}$), 2.22–2.38 (t, C$\underline{H}_2^{e}$), 3.98–4.09 (t, C$\underline{H}_2^{i}$), 4.10–4.15 (t, C$\underline{H}^{o}$), 4.91–4.96 (m, C$\underline{H}^{b}$), 5.48 (s, C$\underline{H}^{s}$), 6.03 (s, C$\underline{H}^{t}$).

^{13}C NMR (CDCl$_3$): δ (ppm) = 18.3 (C^{u}), 22.1 ($C^{a,\,a'}$), 24.6 ($C^{g,m}$), 25.5 ($C^{f,l}$), 28.4 (C^{h}), 30.9 (C^{n}), 34.1 (C^{e}), 34.4(C^{k}), 42.4 (C^{b}), 64.2 (C^{i}), 64.3 (C^{b}), 67.7 (C^{o}), 125.3 (C^{q}), 136.5 (C^{r}), 167.5 (C^{p}) 173.1 (C^{c}), 173.6 ($C^{d,j}$).

Synthesis of Graft Copolymer: poly(methacryl-g-caprolactone)

- By conventional free radical polymerization

A typical copolymerisation using MMA to ω-MPCL molar ratio 98:2 is described here: ω-MPCL (0.10 g, 0.044 mmol) and MMA (0.215 g, 2.15 mmol) were dissolved in toluene (1.1 mL) in a glass tube equipped with a Rotaflo. AIBN (1 mol%,) was added and the mixture was degassed by three freeze-pump-thaw cycles. The polymerization was carried out at 70 °C for the required time. The crude polymer obtained was analysed by ^{1}H NMR and was then precipitated in methanol to eliminate unreacted monomer. The graft copolymer (Figure 11) was dried under vacuum and characterized by ^{1}H NMR and ^{13}C NMR.

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.81–1.03 (3H, C$\underline{H}_3^{q,n}$), 1.21–1.24(d, 2C$\underline{H}_3^{a,a'}$), 1.3-7-1.44 (m, 2H, –C$\underline{H}_2^{f}$), 1.60–1.70 (4H, 2C$\underline{H}_2^{e,g}$), 1.72–1.98 (2H, C$\underline{H}_2^{l,o}$), 2.28–2.34 (t, 2H, C$\underline{H}_2^{d}$), 3.59–3.62 (s, 3H, C$\underline{H}_3^{j}$), 4.03–4.08 (t, 2H, C$\underline{H}_2^{h}$), 4.89–4.97 ($\underline{H}^{b}$).

^{13}C NMR (CDCl$_3$):δ (ppm) = 16.7 and 18.9 ($C^{n,q}$), 22.1 ($C^{a,a'}$), 24.8 (C^{f}), 25.7 (C^{e}), 28.5 (C^{g}), 34.5 (C^{d}), 45.1–45.7 ($C^{l,o}$), 52.0 (C^{j}), 53.6–54.7 ($C^{m,p}$), 64.3 (C^{h}), 173.6 (C^{c}), 177.2–178.6 ($C^{i,k}$).

- By ATRP in toluene as solvent

A typical solution polymerization using MMA to ω-MPCL molar ratio 95:5, [M]/[EBBr]/[CuBr]/[bpy] = 100/1/1/2, [M] = 2.0 M is given here.

ω-MPCL (0.30 g, 0.13 mmol) was dissolved in toluene (1.3 mL) and MMA (0.25 g, 2.5 mmol) was added. A solution of EBBr (5 mg, 0.026 mmol), CuBr (4 mg, 0.026 mmol) and 2,2-bipyridine (8.2 mg, 0.053 mmol) in toluene (0.7 mL) was added and the mixture was degassed by three freeze-pump-thaw cycles. Polymerization was carried out at 70 °C and after the desired polymerization time, the crude polymer was precipitated twice in methanol to remove any unreacted monomer. It was then dried under vacuum and characterized by ^{1}H NMR, ^{13}C NMR and SEC. The ^{1}H

and ^{13}C NMR results were similar to those obtained above.

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