Experimental Procedure.

Chemicals. ε-caprolactone was purchased from Sigma Aldrich and dried over CaH_2 for 12 hours, distilled under vacuum and stored over molecular sieves. Styrene was purchased from Sigma Aldrich and stored over molecular sieves. Azobisisobutyronitrile (AIBN) was purchased from Sigma Aldrich and recrystallised twice from cold methanol. *Candida Antarctica* Lipase B (CALB) was purchased in the immobilised form from Novozymes (10 wt% on acrylic resin). CALB is composed of approximately 3 % lysine residues having amine groups which could potentially degrade the thio-moiety of the RAFT agent.

Synthesis of RAFT agent, (2-benzylsulfanyl thiocarbonylsulfanyl)ethanol. 20 mL 2-mercapto ethanol (0.23 mol) was added to potassium hydroxide solution (13 g in 250 mL water, 0.23 mol). 30 mL carbon disulfide was added dropwise and the mixture was stirred for 5 hours. The mixture was then heated for 12 hours at 80 ^oC with 27.5 mL benzyl bromide (39.6 g, 0.23 mol).
Upon cooling, the aqueous phase was extracted with chloroform (300 mL, then 2 x 100 mL) and then dried over magnesium sulfate. The solvent was evaporated and the product redissolved in dichloromethane then run through an aluminium oxide column. The solvent was reduced under vacuum. The product was purified by column chromatography with hexane and ethyl acetate as eluent in the ratio 7:3 to yield a yellow oil. ^1H NMR, $CDCl_3$: 3.59 (t, 2H, CH_2-O), 3.85 (t, 2H, CH_2-S), 4.62 (s, 2H, CH_2-Ph), 7.31 (m, 5H, Ph).

Polymerisation procedure. In all experiments, the molar ratio of RAFT agent to AIBN was kept constant at 2:1. In a typical experiment (Table 1, Entry 4), 0.3 g Novozym-435 (10 wt% with respect to caprolactone) was dried at 40 ^oC under vacuum at < 10 mTorr for 24 hours. 3 mL ε-caprolactone, 3 mL styrene, 50 μL RAFT (2.05×10^{-4} mol) and 16.8 mg AIBN (1.025×10^{-4} mol) was added to the vessel under a constant flow of CO_2 to prevent the ingress of moisture. The autoclave was then heated to 65 ^oC, pressurised to 4000 psi and stirred at 300 rpm for 24 hours. Theoretical M_n for PSTY block: 4300 Da. (For Entry 6, Table 1, 150 μL RAFT and 50.4 mg AIBN was used – Theoretical Mn for PSTY block: 3100 Da).

Theoretical M_n of PSTY = (Molar $mass_{STY}$ x [STY] x $Conversion_{STY}$) / [RAFT]

Nuclear Magnetic Resonance Spectroscopy.

^1H NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300.14 MHz for protons. The mole fraction of PSTY and PCL in the copolymer was measured using ^1H NMR spectroscopy by comparing the integral of the PCL signal at 4.05 ppm (CH_2-O) and the PSTY signal at 6.60 ppm (CH_2).

Determination of end-groups. The end-groups were determined by oxalyl chloride treatment of the terminal hydroxyl functionalities (Fig. S1). Upon treatment with oxalyl chloride, downfield shifts of all neighbouring protons were observed. The peak at 3.65 ppm (H_a) shifted to 4.37 ppm ($H_{a'}$). This was assigned to the methylene protons adjacent to the hydroxyl chain end. Additionally, a new peak was observed at 2.90 ppm ($H_{b'}$) upon reaction with oxalyl chloride and was assigned to the methylene protons adjacent to the carboxylic end group. This peak was unresolved in the original

spectrum (Fig. S2). Characterisation by this procedure has been reported previously (Villarroya et al. Macromolecules **2006**, *39*, 633).

The amount of PCL that was initiated by water was calculated by comparing the integral of the peak at 4.37 ppm (terminus of all PCL in the mixture) and the peak at 2.90 ppm (terminus of water initiated PCL). Treatment with oxalyl chloride showed that almost all of the PCL was initiated with the RAFT agent.

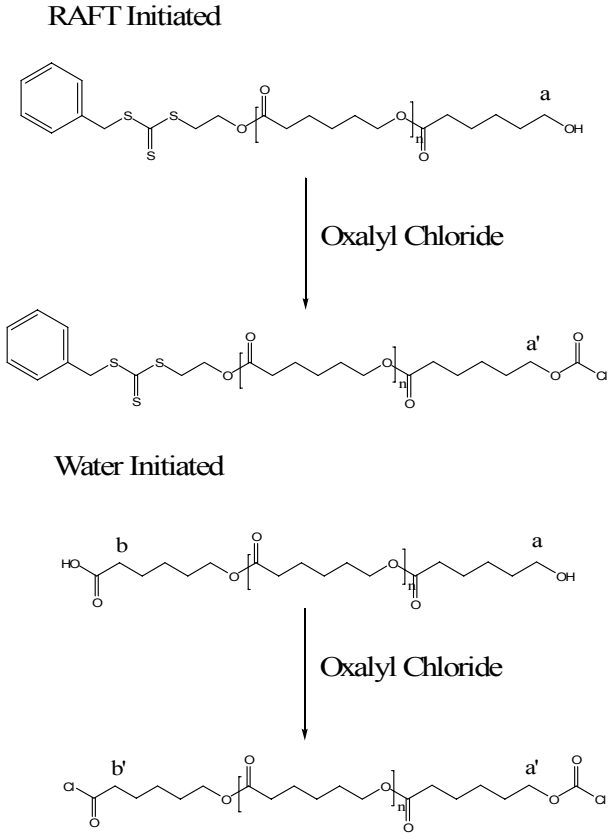

Fig. S1. Structure of the RAFT and water initiated PCL before and after treatment with oxalyl chloride.

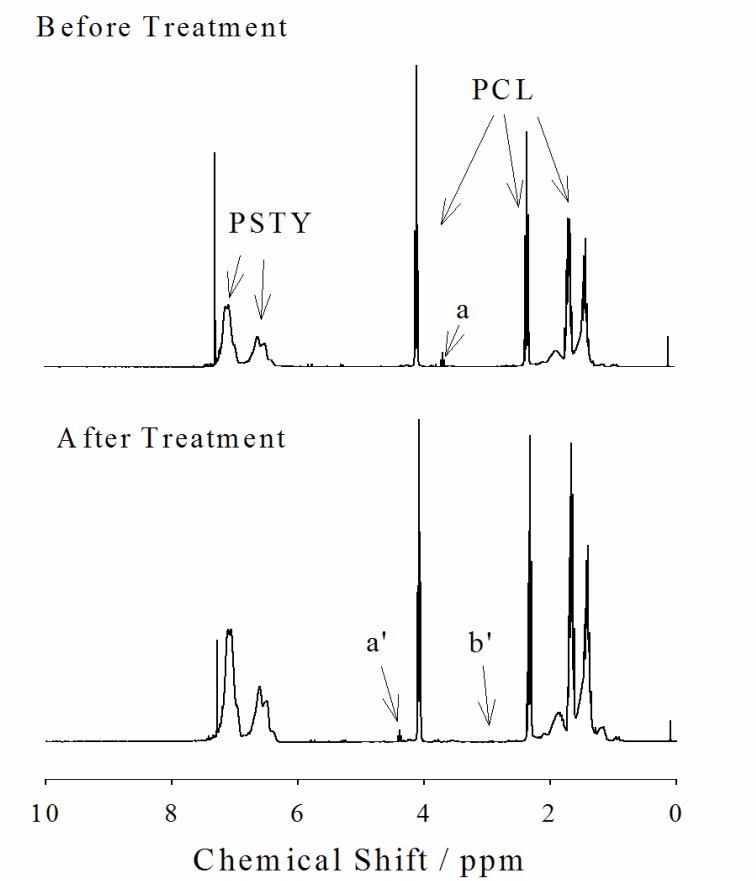

Fig. S2. ^{1}H NMR spectrum of PSTY-block-PCL before and after treatment with oxalyl chloride. The very low concentration of carboxylic acid end groups (b') indicates that the incidence of water initiated PCL is very low.

MALDI-TOF MS

MALDI-TOF Mass Spectrometry was carried out at the EPSRC National Mass Spectrometry Service Centre, Swansea. The samples were analysed using a Voyager-DE-STR spectrometer, with dithranol as matrix and $AgNO_3$ as cation.

An example of the MALDI spectrum acquired for the copolymer (Table 1, Entry 5) in reflectron mode is shown in Figure S3. A number of mass series are present in the spectrum, leading to a complicated mass pattern. Peaks pertaining to copolymer are clearly evident and exhibit isotopic splitting patterns expected for the copolymer species. Additionally, mass differences between series of 10 Da are observed. This is indicative of the mass difference between ε-CL and STY monomer units. Assignments of the respective series are presented (Table S1).

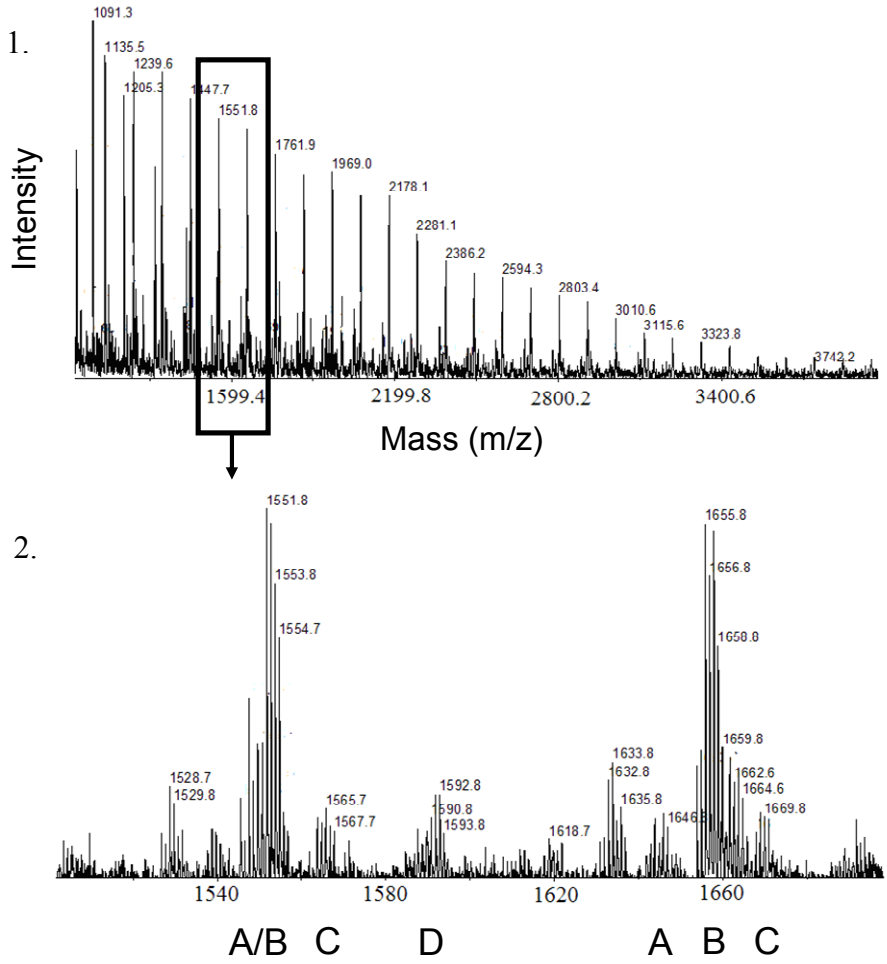

Fig. S3. MALDI-TOF mass spectrum of block copolymer (1) with low molecular weight (Mn = , PDI =) and an expansion of the mass series between 1500-1700 Da (2). Series A, B and C are assigned to copolymer series while series D is assigned to cyclic PCL.

Table S1. Molecular weight of PCL-*b*-PMMA and cyclic PCL by theoretical calculation and MALDI-TOF MS

Series	Polymer Chain[a]	[a]Calculated Mwt (Da)	Detected Mwt (Da)
A[a]	7 CL + 4/5 STY	1543.7 / 1647.9	1545.5 / 1647.9
B[a]	8 CL + 3/4 STY	1553.7 / 1657.9	1551.8 / 1658.8
C[a]	9 CL + 2/3 STY	1563.7 / 1667.9	1565.7 / 1667.8
D	13 CL cyclic	1590.7	1590.8

[a]Mass calculated with addition of RAFT agent, initiator-terminated PSTY, H-terminated PCL and Ag^+ ion.

Hydrolysis of copolymer

In a typical hydrolysis reaction, 1 g of copolymer was dissolved in 18 mL Dioxane and 1.5 mL 30 wt % HCl and reacted at 85 ^{o}C for 18 hours. The product was precipitated in cold methanol and NMR was used to test for the absence of PCL in the polymer. The GPC trace of the hydrolysed product was always at longer retention time than the copolymer (Figure S3) indicating that the copolymer had been formed.

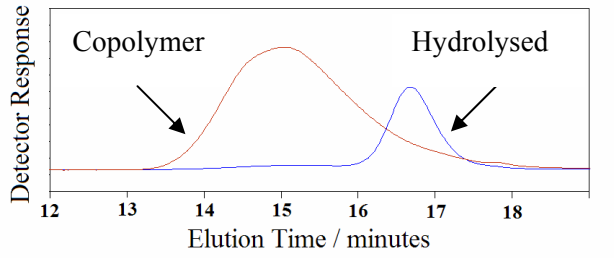

Fig. S4 GPC traces of copolymer and the hydrolysed product. The hydrolysed product is clearly of lower molecular weight than the original copolymer.

Gradient Polymer Elution Chromatography (GPEC).

GPEC was performed using a PLRS 300 column (Polymer Laboratories) with a mixture of methanol and tetrahydrofuran as the mobile phase. An ELS-1000 detector (Polymer Laboratories) was used to determine the elution time of each polymer. In a typical experiment, 5 mg of sample was dissolved in 1 mL of 1:1 mixture of tetrahydrofuran and methanol and 20 µL of the solution was adsorbed onto the column. The column was flushed for 5 minutes with 99% methanol followed by a tetrahydrofuran gradient to 99% for 15 minutes. Finally, the column was washed for 5 minutes with 99% tetrahydrofuran (Fig. S5).

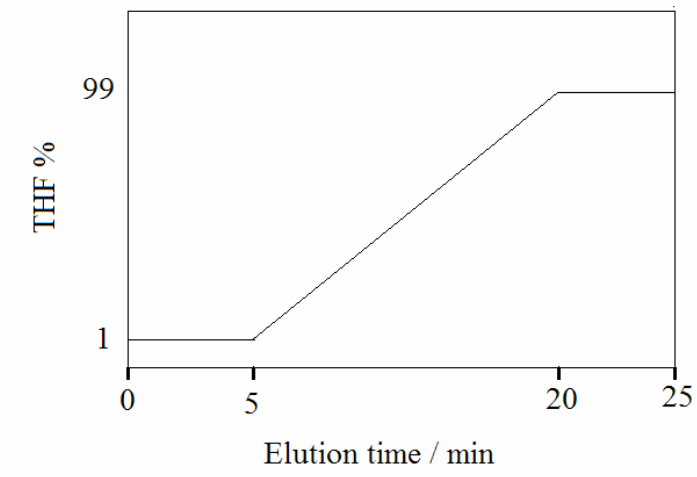

Fig. S5. Gradient program for GPEC experiments using tetrahydrofuran and methanol.