Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information for:

Side-chain functionalisation of unsaturated polyesters from ring-opening polymerisation of macrolactones by thiol-ene click chemistry

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Experimental

Materials

Globalide was provided by Symrise. Novozyme 435 (*Candida Antarctica* Lipase B immobilised on cross-linked polyacrylate beads) was purchased from Novozymes A/S and dried over a molecular-sieve under vacuum. Butyl 3-mercapto propionate and 6-mercapto 1-hexanol were purchased from Sigma-Aldrich and used without further purification. Toluene was dried over aluminium oxide. All other reagents and solvents used were purchased from Sigma-Aldrich and used without further purification.

Methods

Gel Permeation Chromatography (GPC) measurements for all samples were performed using an Agilent 1200 series instrument equipped with GPC control software. All measurements were carried out using a Polymer Laboratories Gel 5 µm Mixed-C 300x7.5 mm column, at 40 °C. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min. The molecular weights of all polymers were calculated based on polystyrene standards. ^{1}H NMR spectra was recorded using Bruker Avance 400 MHz spectrometer with $CDCl_3$ employed as the solvent in all experiments. Differential Scanning Calorimetry (DSC) measurements were performed on a TA Instruments Q200 DSC at a heating rate of 10 °C per minute.

Synthesis of Polyglobalide via Enzymatic Ring Opening Polymerization

Novozyme 435 (0.44 g) was dried in a Schlenk flask over a molecular-sieve at 40 °C in a vacuum oven overnight. Globalide (2.1 g) and dried toluene (2.0 g) were then added to reaction flask which was then purged with nitrogen gas before being heated in an oil bath set at 60 °C. After four hours, dichloromethane (DCM) was added to the reaction mixture to dissolve the product and inhibit enzyme activity. The product was isolated from the solution by precipitation in ice-cold methanol. The resultant polymer was dried overnight at room temperature under vacuum. Yield: 60%.

Synthesis of Thiol Functionalised Polymers (Optimum Conditions)

PGl-B3MP

Polybglobalide (0.1 g) and butyl 3-mercapto propionate (0.1 g) were weighed into a Schlenk flask and AIBN (10 mg) was added. The reaction flask was then purged with nitrogen gas. The reaction was started by immersing the reaction flask into an oil bath at 80 °C; solution agitation was provided by magnetic stirring. The reaction was allowed to run for 24 h. Yield: Could not be determined due to large polydispersity of the product.

PGl-6MH

Polybglobalide (0.2 g) and 6-mercapto 1-hexanol (0.5 g) were weighed into a Schlenk flask in the presence of AIBN (10 mg). 1 mL of THF was added and the reaction flask was purged with nitrogen gas. The reaction commenced by immersing the reaction flask into an oil bath at 80 °C; solution agitation was provided by magnetic stirring. The reaction was allowed to run for 24 h. Yield: 65%

PGl -nACA

Polybglobalide (0.2 g) and N-acetylcysteamine (0.78 g) were weighed into a Schlenk flask in the presence of AIBN (50 mg). 1 mL of THF was added and the reaction flask was purged with nitrogen gas. The reaction commenced by immersing the reaction flask into an oil bath at 80 °C; solution agitation was provided by magnetic stirring. The reaction was allowed to run for 24 h. Yield: 82%

All three reactions were terminated by the addition of DCM to the reaction mixture immersed in an ice bath. The products were precipitated with ice-cold methanol and the solvents gently removed by rotary evaporation. The obtained polymers were dissolved in DCM before being reprecipitated. This procedure was repeated a further two times. The final polymers were dried overnight under vacuum at room temperature prior to further analysis.

Coupling Yield Vs Solvent Concentration

The amount of THF added strongly influences the thiol-ene coupling efficiency.

PG-nACA Optimisation

Table S1: The variation in thiol-ene coupling efficiency of MH to PGl in response to varied solvent concentrations.

	PGl	**PGl-MH**		
MW (g/mol)	1.6x10^4	2.08x 10^4	2.27x10^4	2.49x10^4
Polydispersity	2.53	2.22	1.88	3.66
T$_m$	48 °C	-	-	-
Thiol-ene coupling (%)	-	≥ 95	80-94	47
Reaction Details		*0.6 mmol PGl* *Double Bonds* [a] *4 mmol MH* *1 mL THF* *10 mg AIBN*	*0.6 mmol PGl* *Double Bonds* [a] *4 mmol MH* *bulk* *10 mg AIBN*	*0.6 mmol PGl* *Double Bonds* [a] *4 mmol MH* *10 mL THF* *10 mg AIBN*

[a] The concentration of PGl double bonds was estimated from the molecular weight of the polymer as determined by GPC with poly(styrene) calibration.

Table S2: Experimental parameters were altered to determine a method for the optimal nACA functionalisation of PGl.

	PGl	**PGl-nACA**						
MW (g/mol)	1.6x10^4	1.83x 10^4	1.85x10^4	1.28x10^4	1.56 x10^4	2.19 x10^4	2.09x10^4	2.35x10^4
Polydispersity	2.53	2.08	1.87	2.36	1.93	1.65	1.84	1.82
T_m (°C)	48	-	-	-	-	-	-	-
Thiol-ene coupling (%)	-	17	44	55	86	73	60	≥ 95
Reaction Details		*0.6 mmol PGl Double Bonds*[a] *0.4 mmol nACA* *Bulk Reaction* *10 mg AIBN*	*0.6 mmol PGl Double Bonds* [a] *1.6 mmol nACA* *Bulk Reaction* *10 mg AIBN*	*0.6 mmol PGl Double Bonds*[a] *1.6 mmol nACA* *1 mL THF* *10 mg AIBN*	*0.6 mmol PGl Double Bonds* [a] *3.2 mmol nACA* *Bulk Reaction* *10 mg AIBN*	*0.6 mmol PGl Double Bonds* [a] *6.6 mmol nACA* *Bulk Reaction* *10 mg AIBN*	*0.6 mmol PGl Double Bonds* [a] *6.6 mmol nACA* *1 mL THF* *10 mg AIBN*	*0.6 mmol PGl Double Bonds* [a] *6.6 mmol nACA* *1 mL THF* *50 mg AIBN*

[a] The concentration of PGl double bonds was estimated from the molecular weight of the polymer as determined by GPC with poly(styrene) calibration.