Supplementary Material (ESI) for Chemical Communications

Synthesis of Well-Defined Locust Bean Gum-graft-Copolymers using ambient aqueous Atom Transfer Radical Polymerisation

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Supplementary Information

Typical preparation for LBG macroinitiators

A 6% w/v solution of lithium chloride (LiCl) in N,N-dimethylsulfoxide (DMSO) was prepared by heating 30g of LiCl in 500cm^3 of anhydrous DMSO to 150°C in a 2-necked round bottom flask fitted with an overhead stirrer. Once a homogeneous solution had been obtained, Locust Bean Gum (Meyprodyn 200 ex Rhodia) (30g, 0.185 mol of anhydromannose/galactose unit) was added to the solution gradually, maintaining the temperature at 150°C until a highly viscous, clear, yellow solution had formed. The solution was cooled to 65°C. In a separate beaker, a solution of 2-bromoisobutyric acid (45g, 0.27mol) in DMSO (50cm^3) was prepared. To this solution, a solution of 1,1'-carbonyldiimidazole (CDI) (45g, 0.278 mol) in anhydrous DMSO was added slowly. Once the evolution of CO_2 had ceased, this solution was added to the LBG/DMSO/LiCl mixture with stirring. The reaction was maintained at 65°C for 24 hours before pouring into a threefold volume of methanol, causing the product to precipitate. The product was collected on a sinter funnel, re-dispersed into methanol, filtered and washed with copious amounts of methanol before being subjected to soxhlet extraction (methanol) for 48 hours and dried *in vacuo* at 60°C for a further 48 hours, yielding 26.4g of a creamy coloured, crystalline solid.

IR: 1736 cm^{-1} (s, saturated ester carbonyl); **NMR (^{1}H-$D_2$0)**: 1.84 (d, ester CH_3, 6H); 3.4-4.6 (bm, mannose/galactose CH and CH_2); **NMR (^{1}H-DCl/$D_2$0)**: 1.79 (d, ester CH_3, 6H); 3.4-4.2 (bm, mannose/galactose CH and CH_2, 64H); 4.6-5.4 (bm, anomeric H, 10H)

Preparation of Locust Bean Gum macroinitiators for polymerisation:

The required LBG- macroinitiator was weighed into a glass screw-cap bottle and filled with the appropriate amount of demineralised water to give a solid content of 10%. This solution was left to roller, using a conventional bench roller, overnight at ambient temperature to ensure complete dissolution of the macroinitiator.

General procedure for a graft-copolymerisation:

To a 3-necked round bottom flask fitted with a N_2 inlet, thermometer and suba seal, fitted with a syringe needle, were added the dissolved LBG – macroinitiator and the required monomer. The resulting solution was de-gassed by bubbling nitrogen gas for 45 minutes. Copper (I) bromide and 2,2'-dipyridyl were added to the reaction flask as a mixture of solids. A polymerisation exotherm of 2-3^{o}C was noted in some cases. The reaction was stirred for 4 hours at ambient temperature. The contents of the flask were then diluted with demineralised water and the solution passed through a sintered glass funnel (pore size 2) containing a bed of wet silica or activated, basic aluminium oxide, attached to a Buchner flask. The filtrate was added to a 3 fold volume of methanol, causing the product to precipitate. The polymer was collected on a filter and dried in vacuo at 40^{o}C to constant weight.

Characterisation Methods

^{1}H-NMR Spectroscopy

Standard qualitative and quantitative experiments were performed using a Bruker 500 MHz spectrometer. Samples were prepared either as polymer solutions in D_2O containing 0.05% 3-(trimethylsilyl)propionic acid, sodium salt (TSP) as the internal standard or, prior to analysis, the sample was de-polymerized by acid hydrolysis using a solution of 20% DCl in D_2O and heating for 1.25 hour at 70^{o}C. Signals are quoted in parts per million (ppm) relative to TSP.

Two example spectra are shown in Figure 1 comparing the macroinitiator before and after acid degradation.

NMR analysis of LBG-graft-copolymers

Once the Cu catalyst has been removed, the polymer solution is freeze-dried and analysed. ^{1}H-NMR using D_2O as the solvent provides information of the success of the graft-polymerisation. For more accurate, quantitative analysis, the polysaccharide graft copolymer is degraded using 20% v/v DCl/D_2O for 1.25 hour at 70^{o}C. Example ^{1}H-NMR spectra of LBG-graft-PEGmethacrylate are shown in Figure 2.

Spectrum (a) has the following peak assignments: 0.8-2.4 ppm (bm, vinylic polymer backbone); 3.4 ppm (s, PEG monomethoxy CH_3); 3.5-4.5 ppm (bm, mannose/galactose CH and CH_2; PEG CH_2). The signals due to the PEG CH_2 protons overlap with the signals due to the LBG ring CH and CH_2 protons. The integral due to the LBG ring protons can still be calculated by using the intensity from the PEG methylenes

Integral region A (0.8-2.4 ppm) = 5 x ^{1}H ex methacrylate component (i)
Integral region B (3.5-4.5 ppm) = 28 x ^{1}H ex PEG side chain + integral due to LBG ring protons (ii)
Therefore, integral due to LBG ring protons = B - (A/5 x 28)
= 14.4 – (1.9/5 x 28)
= 3.8

Since the degree of substitution of the LBG-macroinitiator is known from previous NMR analysis, the integral due to the LBG ring protons can be divided by the number of contributing nuclei (for this example, the number of protons per repeat unit for the LBG macroinitiator is (12 x 6) = 72).

Therefore, integral/proton for LBG ring = 3.8/72
= 0.05
From (i),
the integral/proton for the methacrylate backbone = 1.8/5
= 0.36
Therefore, the molar ratio of PEGmethacrylate:LBG ring = 0.36/0.05
i.e. the degree of polymerisation of PEG methacrylate = **7**

By comparison, the ^{1}H-NMR spectrum (b) of LBG-graft-PEGmethacrylate (after DCl/D_2O degradation) gives the following peak assignments: 0.8-2.2 ppm (bm, vinylic polymer backbone); 3.4 ppm (s, PEG monomethoxy CH_3); 3.5-4.3 ppm (bm, mannose/galactose CH and CH_2; PEG CH_2); 4.6-5.4 ppm (m, anomeric Hs).

The integration of the peaks due to the LBG anomeric protons (region C) can be set to 1, as there is only one anomeric proton per LBG ring.

Integration of the main peak regions allows the length of the PEGmethacrylate graft to be calculated in exactly the same way as described in the above example:

Integral region A (0.8-2.2 ppm) = 5 x ^{1}H ex methacrylate component (iii)

Integral region B (3.5-4.3 ppm) = 28 x ^{1}H ex PEG side chain + integral due to LBG ring protons (iv)

Therefore, integral due to LBG ring protons = B - (A/5 x 28)
= 16.4 – (2.22/5 x 28)
= 4.4

Again, since the degree of substitution of the LBG-macroinitiator is known, the integral due to the LBG ring protons can now be divided by the number of contributing nuclei (for this example, the number of protons per repeat unit for the LBG macroinitiator is (12 x 6) = 72).

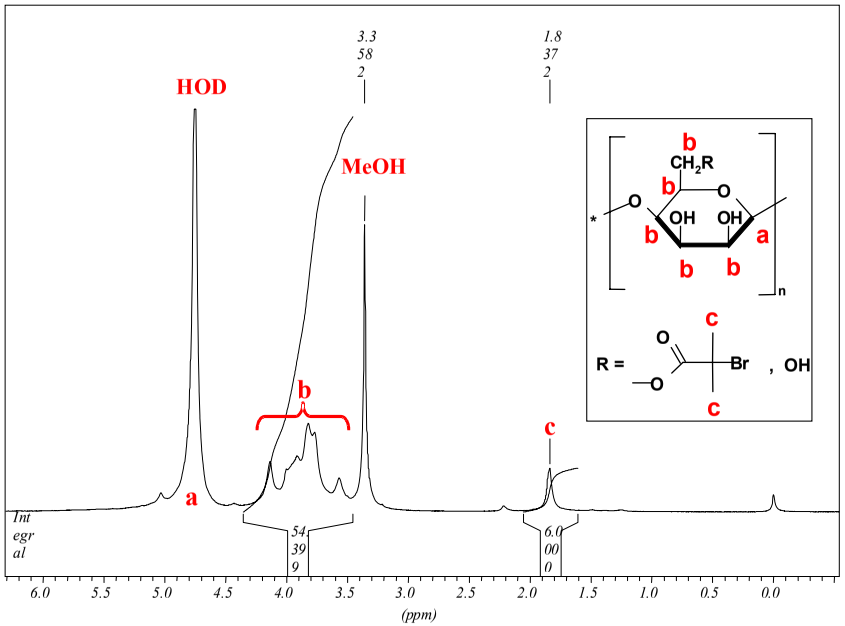
Therefore, integral/proton for LBG ring = 4.4/72
= 0.061

From (iii), the integral/proton for the methacrylate backbone = 2.22/5
= 0.43

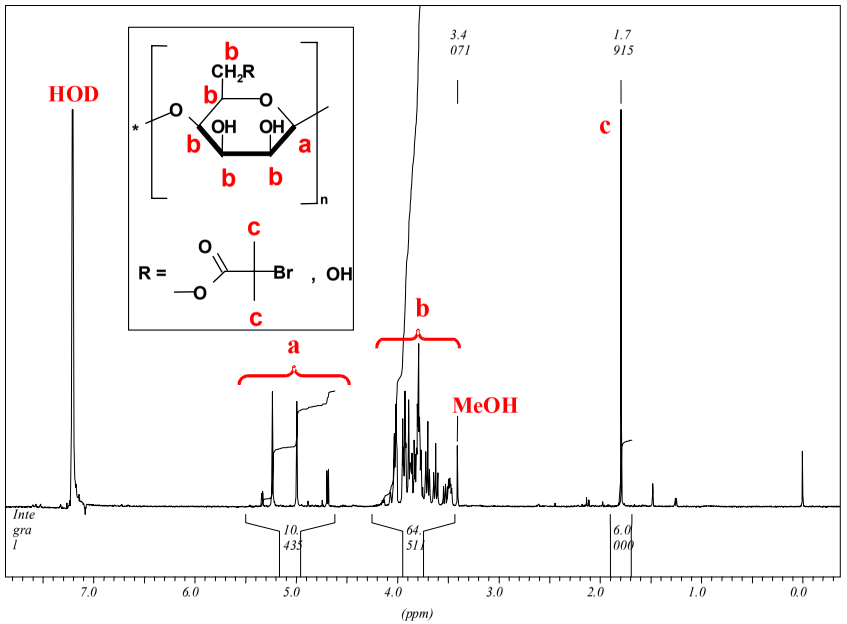
Therefore, the molar ratio of PEGmethacrylate : LBG ring = 0.43/0.061

i.e. the degree of polymerisation of PEG methacrylate = **7**

Figure 1

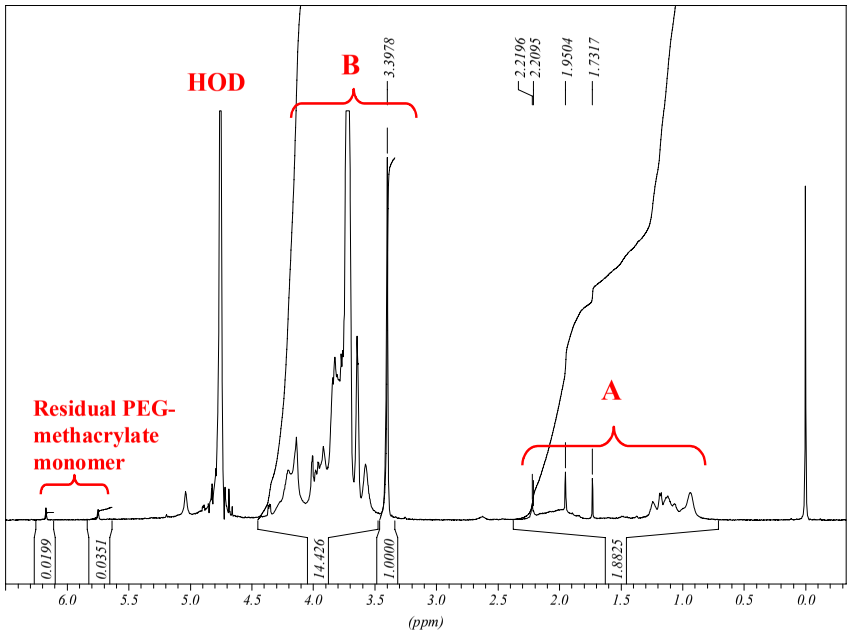


^{1}H-NMR spectrum of LBG-initiator in D_2O

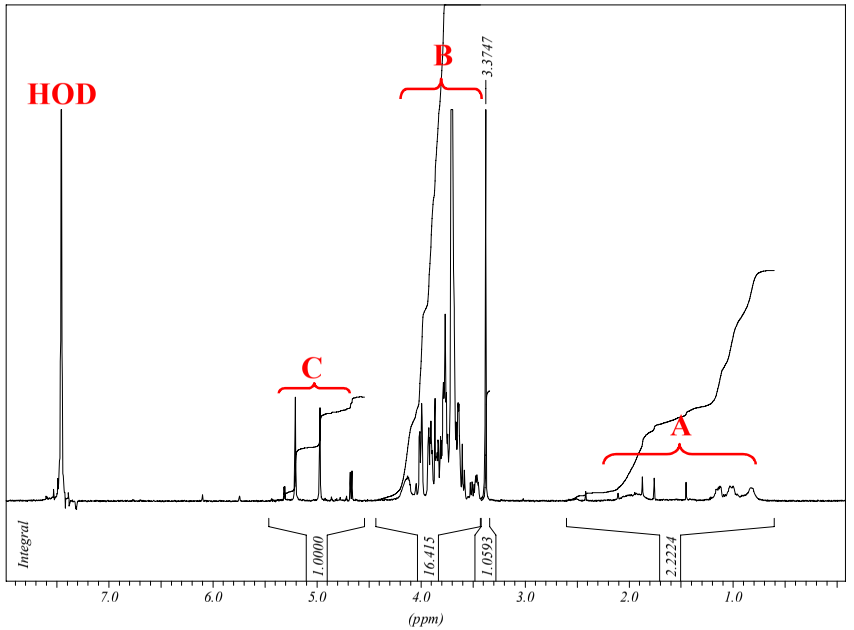


^{1}H-NMR spectrum of LBG-initiator after 20% DCl/D_2O degradation

Figure 2



a) ^{1}H-NMR spectrum of LBG-graft-monomethoxypoly(ethyleneglycol methacrylate) in D_2O



b) ^{1}H-NMR spectrum of LBG-graft-monomethoxypoly(ethyleneglycol methacrylate) in 20% DCl/D_2O

Infrared Spectroscopy
Infrared spectrometry was carried out on a Bio-Rad 175C FT-IR spectrometer using a Specac Golden Gate Horizontal ATR cell.

Example IR spectrum comparing LBG before and after macroinitiator synthesis

Size Exclusion Chromatography-Multi Angle Laser Light Scattering (SEC-MALLS)
Aqueous polysaccharide solutions (0.2% w/w) were analysed using a TSK GMPW column with an eluent of 0.05M $NaNO_3$/1M NaOH/20% MeOH and a flow rate of 0.8ml/min. Detectors were a Water 410 IR followed by a Dawn DSP light scattering detector. The data were analysed using 'Astra' software. The dn/dc value used for all data was 0.135ml/g.