

Quantitative formation of core cross-linked star polymers via a one-pot two-step single electron transfer-living radical polymerization

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Copper (II) bromide (Cu(II)Br₂, 99%, Aldrich), *tert*-butyl α -bromoisobutyrate (\geq 98%, Aldrich), tris[2-(diethylamino)ethyl] amine (Me₆TREN, Aldrich) were used as received. Monomers methyl acrylate (MA, 99%, Aldrich) and ethylene glycol diacrylate (EGDA, 90%, Aldrich) were de-inhibited by percolating over a column of basic alumina prior to use. The solvents dimethyl sulfoxide (DMSO), hexane, diethyl ether (DEE), tetrahydrofuran (THF), dimethylformamide (DMF) and methanol (MeOH) were obtained from Chem-Supply and used as received. Deuterated chloroform (CDCl₃) was obtained from Cambridge Isotope Laboratories and used as received. Copper wire (0.315 mm diameter) was activated by immersion in concentrated sulfuric acid for 10 min. The wire was washed thoroughly with distilled water before it was dried under a stream of Ar. Freshly activated Cu wire was used immediately for every reaction.

Methods

Macroinitiator and CCS Formation in One Pot

In a typical reaction, a solution of MA (4.73 mL, 52.5 mmol), Cu(II)Br₂ (5.9 mg, 26.3 μ mol), Me₆TREN (25 μ L, 94.6 μ mol) and *tert*-butyl α -bromoisobutyrate (98 μ L, 525 μ mol) dissolved in DMSO (4.73 mL) was bubbled with N₂ gas for 30 min. The molar ratio of the reactants was as follows: [monomer]/[initiator]/[Cu(II)]/[ligand] = [100]/[1]/[0.05]/[0.18]. Copper wire (*ca.* 4 cm in length) was added to the mixture and the flask was kept under a N₂ atmosphere with stirring at RT to react for 2 h. 100 μ L aliquot of the macroinitiator (**P1**) solution was taken for NMR and GPC analysis. To induce star formation, an EGDA solution in DMSO (that has been degassed with N₂ beforehand) was transferred to the reaction flask containing the macroinitiators using a double-tipped canula under a N₂ blanket. The reaction was stirred at RT for a further 16 h. The amount of cross-linker and DMSO solvent added to generate the CCS polymers **CCS1-4** was as follows: **CCS1** (454 μ L cross-linker, 33.1 mL DMSO), **CCS2** (907 μ L cross-linker, 33.1 mL DMSO), **CCS3** (1.36 mL cross-linker, 33.1 mL DMSO), **CCS4** (907 μ L cross-linker, 14.2 mL DMSO). Similar reaction conditions were employed in the synthesis of macroinitiator **P2** but at half the monomer and solvent content (i.e., 2.37 mL of MA and 2.37 mL of DMSO). In making **CCS5**, 680 μ L of EGDA in 16.6 mL of DMSO was added to the **P2** reaction pot after 2 h and the solution was stirred at RT for a further 16 h. 100 μ L aliquots of all crude star samples were taken for NMR and GPC analysis. At the end of the reaction, all star polymers were precipitated into a 1:1 water:MeOH mixture and isolated by centrifugation. The majority of the copper complexes were removed as indicated by the blue color of the supernatant. The precipitates were washed

briefly with DEE and then redissolved in THF, followed by a second precipitation into a 7:3 DEE:hexane mixture. The CCS polymers were dried *in vacuo* prior to GPC analysis. It is important to note that the GPC analysis of the purified and crude star polymer samples reveal identical molecular weight distributions.

Characterization

60 Gel-Permeation Chromatography (GPC)

Polymer molecular weight characterization was carried out via GPC using DMF as the mobile phase. The GPC analysis was conducted on a Shimadzu liquid chromatography system equipped with a PostNova PN3621 MALS detector (λ = 532 nm), Shimadzu RID-10 refractometer (λ = 633 nm) and Shimadzu SPD-20A UV-Vis detector using three identical Jordi columns (5 μ m bead size, Jordi Gel Fluorinated DVB Mixed Bed) in series operating at 70 °C. DMF with 0.05 mol.L⁻¹ LiBr (> 99%, Aldrich) was employed as the mobile phase at a flow rate of 1 mL.min⁻¹. NovaMALS software (PostNova Analytics) was used to determine the molecular weight characteristics using calculated dn/dc values.

Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H NMR spectroscopy was conducted on a Varian Unity 400 MHz spectrometer operating at 400 MHz, using the deuterated solvent (CDCl₃) as reference and a sample concentration of approximately 20 mg.mL⁻¹.

Calculation of CCS average number of arms (N_{arms})

The average value of macroinitiator incorporated into the CCS polymers (N_{arms}) was calculated using **Equation S1**:¹

$$N_{arms} = \frac{WF_{arms} \times M_{w,CCS}}{M_{w,arms}} \quad (S1)$$

where the CCS molecular weight ($M_{w,CCS}$) and the molecular weight of the linear arms ($M_{w,arms}$) were determined by GPC. The weight fraction of arms (WF_{arms}) was determined using **Equation S2**:

$$WF_{arms} = \frac{m(arms)x_a}{m(XL)x_c + m(m)x_m + m(arms)x_a} \quad (S2)$$

where the conversion of cross-linker (x_c) and left-over monomer from the synthesis of the macroinitiator (x_m) were determined by NMR and the conversion of arm (x_a) was determined by GPC analysis of the DRI chromatogram. $m(arms)$, $m(m)$ and $m(XL)$ are the amount (in g) of the macroinitiator, left-over monomer and cross-linker employed in the CCS polymer synthesis. The weight percentage of the core ($Core_{wt\%}$) was subsequently determined via **Equation S3**:

$$Core_{wt\%} = (1 - WF_{arms}) \times 100\% \quad (S3)$$

Notes and references

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- 1 J. M. Ren, Q. Fu, A. Blencowe, G. G. Qiao, *ACS Macro Lett.*, 2012, **1**, 681.