Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2007

Supplementary information

Synthesis of RAFT agent

Synthesis of 3-benzylsulfanylthiocarbonylsulfanylpropionic acid:
3-mercaptopropionic acid (20 mL, 0.23 mol) was added to Potassium Hydroxide solution (26 g in 250 mL H_2O, 0.46 mol). 30 mL of CS_2 was added dropwise. The orange solution was stirred for a further 5 hours.
39.6 g of benzyl bromide (0.23 mol) was added and the mixture was heated to 80 ºC for 12 hours. Chloroform (300 mL) was added to the cooled mixture and then HCL was slowly added until the organic layer turned yellow. The water layer was extracted with chloroform (2 x 100 mL) and then the organic layers dried over $MgSO_4$. The acid functionalised RAFT agent was purified by chromatography (3:1 hexane – ethyl acetate).
1H NMR: 11.1 ppm (bs – COOH), 7.2-7.3 ppm (m, aromatic), 4.63 ppm (s, S-CH2), 3.64 ppm (t, S-CH2), 2.87 (t, CH2-COOH).

Synthesis of PDMS macroRAFT:
30 g of mono-hydroxy terminated PDMS (3 mmol, Mn = 10 kDa) was mixed with dicyclohexyl carbodiimide (0.64 g, 3.1 mmol) and anhydrous chloroform in molecular sieves (40 mL).
3-benzylsulfanylthiocarbonylsulfanylpropionic acid (1.08 g, 4 mmol) was added to the solution and refluxed for 72 hours. The sieves were removed by filtration and the solution was extracted with H_2O until the water phase was colourless. The solvent was removed under vacuum and then the yellow PDMS-RAFT product was washed with hexane. This solution was dried over $MgSO_4$, filtered and then the product recovered following evaporation of solvent.

Polymer Characterisation

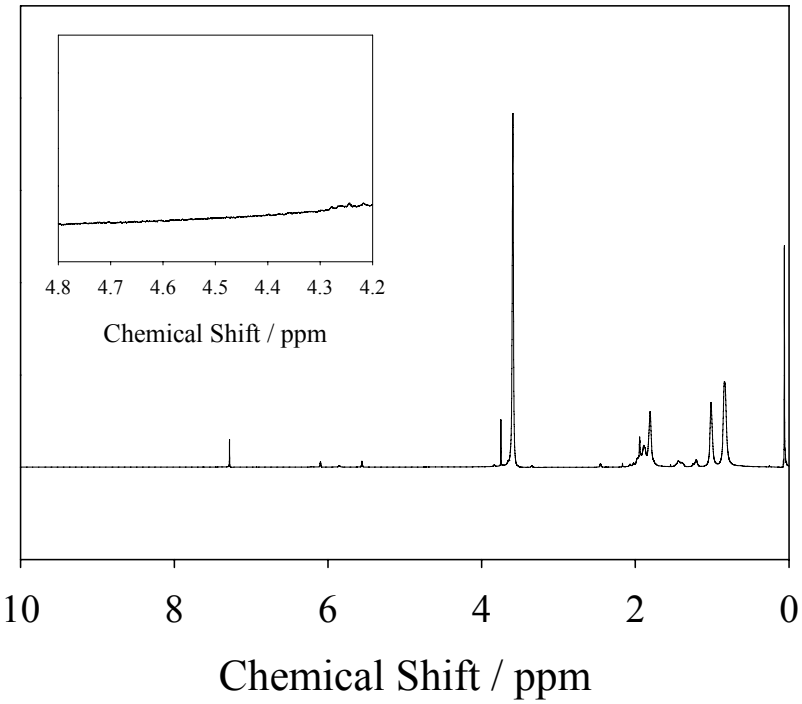
Molecular weight analysis was performed using a PL-120 GPC instrument fitted with an RI detector. The instrument was calibrated with polystyrene standards using THF as eluent.

The molecular weight and polydispersity of the poly(methyl methacrylate) product formed both with and without silver precursor were similar. Note that to obtain the GPC data of the polmer after processing to form Ag nanoparticles, it was necessary to pass these down our GPC columns. ***Even after dissolution in a very good solvent for both PDMS and PMMA (ie. chloroform), intense sonication and then ultracentrifugation, we could not separate the silver from the polymer. This underscores the very strong interaction between the RAFT moiety and the silver nanoparticles. It also shows that if we can't remove the Ag particles, and they remain soluble, then they should pass down the GPC column without causing any damage.***

Details are given in the table below:

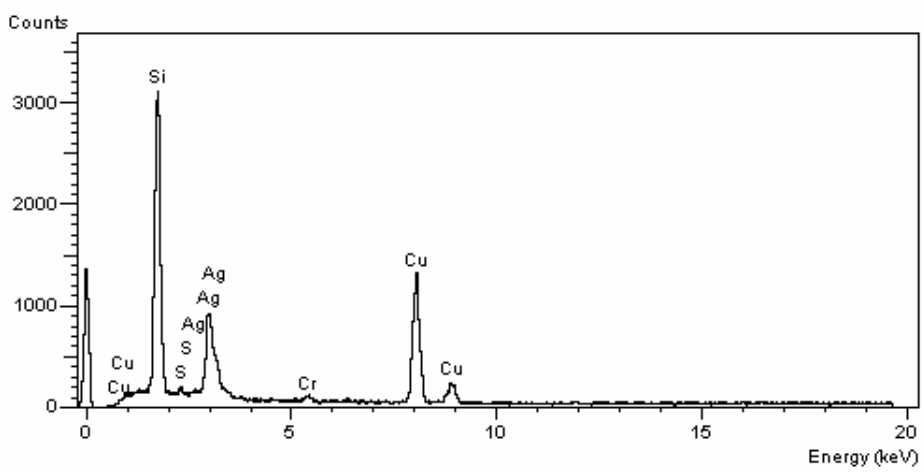
	M_n / kDa	M_w / kDa	PDI
Pure polymer	48	142	2.9
Silver-Polymer nanocomposite	41	130	3.1

NMR analysis was performed using a Bruker DPX300 spectrometer with $CDCl_3$ as solvent. The NMR spectrum for the polymer-silver nanocomposite is shown below with an expansion of the region between 4.2 ppm and 4.8 ppm. The absence of the singlet signal at 4.63 ppm for the methylene protons of the benzyl group of the RAFT agent shows that the stabiliser has been grafted into the polymer through the RAFT agent.



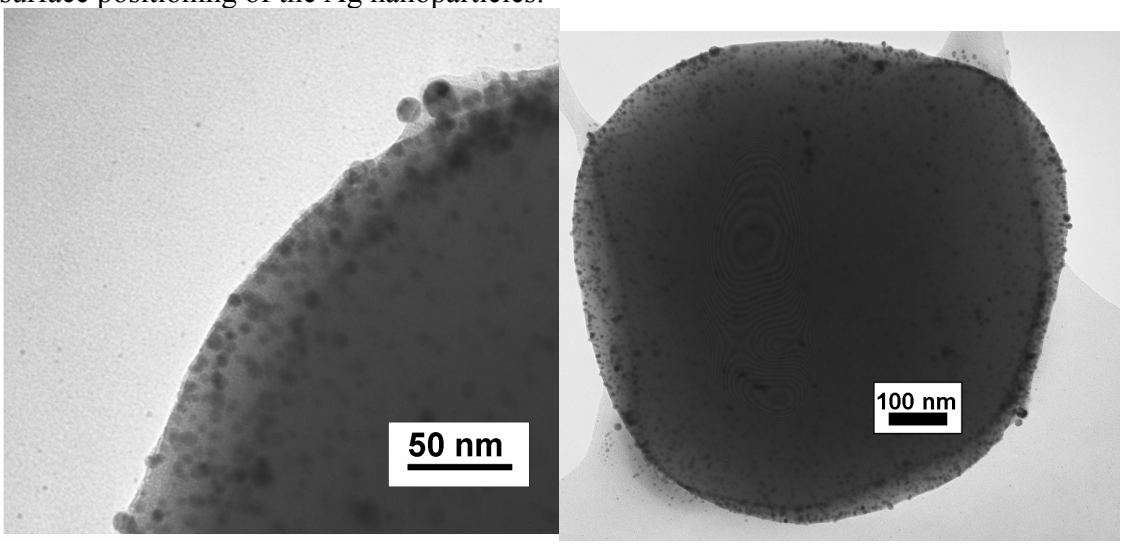
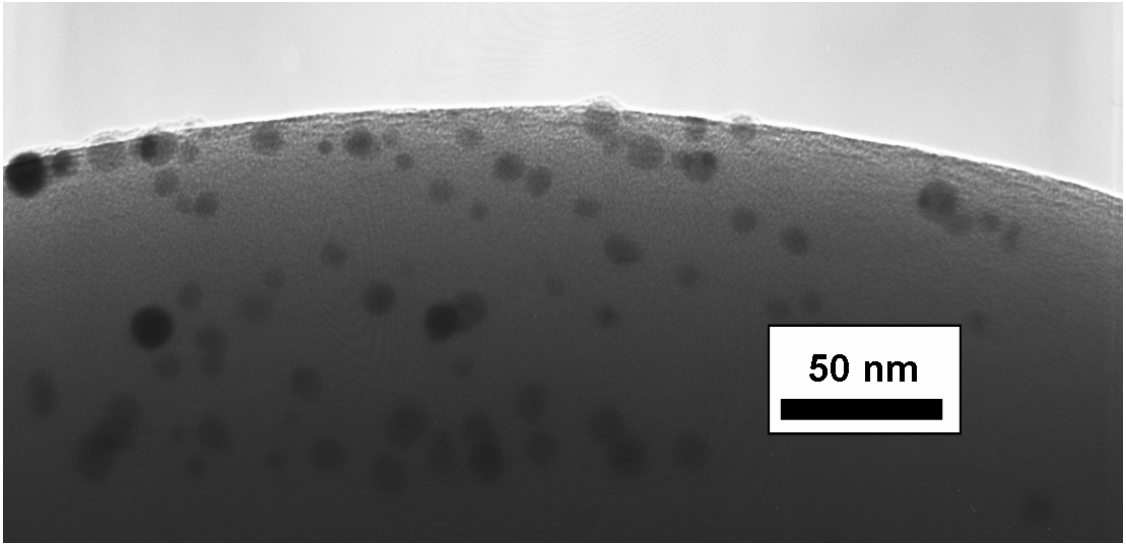
TEM analysis

All TEM analysis was performed with JEOL JEM-200 FXII electron microscope operating at 200 keV. TEM of silver-polymer samples was accomplished by suspending the samples in methanol (with shaking) and placing a drop onto a holey carbon coated copper grid (300 mesh) of 3 mm diameter (Agar Scientific). Thus our analysis was carried out on the whole polymeric microspheres. Energy dispersive x-ray (EDX) analysis measurements were taken during TEM operation.



EDX peaks show silver as well as sulfur and silicon from the RAFT agent and copper from the TEM grid.

We include additional TEM images to supplement the article and to demonstrate the surface positioning of the Ag nanoparticles:



This journal is (c) The Royal Society of Chemistry 2007