

Electronic Supporting Information

Materials

Phenylmagnesium bromide, carbon disulfide, potassium carbonate and iodine (99.999% trace metals basis) were acquired from Sigma Aldrich and were used as received. Methyl methacrylate (MMA) was purchased from Sigma Aldrich and passed through a neutral alumina column and freeze-pump thawed prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN) was purchased from Langfang Triple Well Chemicals Co., Ltd. It was purified by recrystallization in methanol twice. 1H,1H,2H,2H-perfluorooctyl methacrylate (FOMA) as purchased from Fluorochem and used without further purification. Dry CO₂ (99.9%) was purchased from BOC.

Synthesis of RAFT agent.

The RAFT agents were synthesised according to the method of Rizzardo et al.¹ In this procedure, the disulfide of a suitable Z-group for the RAFT agent was reacted with a VAZO compound having the desired R-group for the RAFT agent (eg. AIBN).

Synthesis of Dithiobenzoyl disulfide.

Phenylmagnesium bromide (1 M in THF, 50.0 mL, 5.00 x 10⁻² mol) was added to a round bottomed flask and carbon disulfide (3.30 mL, 5.50 x 10⁻² mol) was added by dropwise. The system was left to stir for 3 hours before removing the solvent under vacuum. A dilute solution of potassium carbonate was then added. An aqueous solution of iodine (0.96 M, 52.0 mL, 5.00 x 10⁻² mol) was added and the disulfide precipitated as pink crystals. These were extracted with dichloromethane and the solvent removed under reduced pressure. The compound was used without further purification.

Synthesis 2-Cyanoprop-2-yl Dithiobenzoate (CPDB)

Dithiobenzoyl disulfide (4.00 g, 1.31 x 10⁻² mol), was added to a round bottom flask with ethyl acetate (30.0 mL) and to this 2,2'-azobis(isobutyronitrile) (AIBN) (2.35 g, 1.44 x 10⁻² mol) was added. The mixture was then heated to 80°C reflux for 18 hours. The solvent was removed under vacuum and the crude product was purified on a silica column (hexane:diethyl ether, 10:3) to yield **3** as a dark red oil. C₁₀H₁₁NS₂; ¹H NMR (CDCl₃) δ (PPM): 1.97 (s, 6H, CH₃), 7.42 (m, 2H, ArH), 7.58 (m, 1H, ArH), 7.93 (m, 2H, ArH).

Synthesis of Poly (1H,1H,2H,2H-perfluorooctyl methacrylate) (PFOMA) macro-RAFT

The PFOMA macroRAFT agents was synthesized using RAFT polymerisation in bulk. The FOMA (5g, 0.0116mol), RAFT agent (CPDB) (0.07g, 3.4×10⁻⁴ M) and

AIBN (10.6 mg, 6.5×10^{-5} M) were put into a 25 mL glass flask with a magnetic stir bar, sealed and then subjected to three freeze-pump-thaw cycles before reaction. The reaction was conducted at 65 °C under a nitrogen atmosphere for 24 h. The polymerization was quenched by cooling down to the room temperature. The polymers were directly used for dispersion experiments without further workup. The molecular weights of PFOMA and conversion were determined by NMR analysis. The cloud point of the macroRAFT agent was measured using a high pressure view cell. RAFT-capped PFOMA having an Mn of 15 kDa was soluble in scCO₂ at 65 °C above 2.8 kpsi (0.75 wt %) and hence was soluble for all reactions conducted in this study.

Dispersion polymerization of MMA

The 60 ml autoclave, and associated piping, was leak tested prior to use with N₂ to 3000 Psi. MMA was degassed via three consecutive freeze-pump-thaw cycles and stored under an argon atmosphere. The 60 ml autoclave was charged with 10.3mg (6.3×10^{-5}) of AIBN and 1.88g (1.25×10^{-4} M) of macro-RAFT agent then purged with CO₂ for 10 minutes before monomer (8 ml (0.075mol)) was introduced under a light flow of CO₂. The autoclave was sealed and pressurized to 800 Psi before being heated up to 65 °C followed by pressurization to the final reaction pressure of 4000 Psi. The reaction proceeded for various times before the heating was turned off and the reaction vessel allowed to cool; the CO₂ reverted to its gaseous state and was vented into the atmosphere. Once atmospheric pressure was reached, the autoclave was opened allowing collection of the final polymerisation product, typically as a free-flowing powder.

1. S. H. Thang; Y. K. Chong; R. T. A. Mayadunne; G. Moad; E. Rizzardo *Tetrahedron Lett.* 1999, **40** (12), 2435.