

Electronic Supplementary Information

Ultra-fast microwave enhanced reversible addition-fragmentation chain transfer (RAFT) polymerization: monomers to polymers in minutes

Steven L. Brown,¹ Christopher M. Rayner,¹ Susan Graham,² Andrew Cooper,²
Steven Rannard^{2,*} and Sébastien Perrier^{1,*}

¹ University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK; *S.Perrier@leeds.ac.uk

² Department of Chemistry, Crown Street, Liverpool, L69 7ZD, UK;

*Steven.Rannard@unilever.com

Experimental conditions for microwave polymerisations

The microwave samples, in each case, were prepared as bulk solutions composed of the ratios described in the main article. They were then decanted into specialised microwave reaction vessels (of approx. volume ~ 20 ml.), septum sealed and deoxygenated by purging with nitrogen for 5 minutes. The methyl acrylate and vinyl acetate samples were deoxygenated over a dry-ice acetone slurry (due to the volatilities of both monomers). The styrene samples were sufficiently deoxygenated over an ice water slurry. The microwave used was a CEM Discover BenchMate. A maximum power setting of 300 watts and a pressure cut-off limit of 220 p.s.i. was set. The ramp time (the maximum time the microwave has to reach the desired temperature from ambient) was set to 5 minutes and the appropriate times and temperatures required were entered manually. A “power-maximum” function was utilised whereby the sample was cooled by compressed air to keep the temperature low whilst increasing the microwave power. The compressed air was set at a maximum pressure of 20 p.s.i. At the end of the reaction, samples were removed from the microwave and plunged into iced water to quench the reaction prior to analysis.

In contrast to experiments performed without the use of compressed air, the microwave power was continuous at a high output for the duration of the reaction. As shown in Figures 1-3, the temperature of the reaction vessel is not compromised with the increase in microwave power.

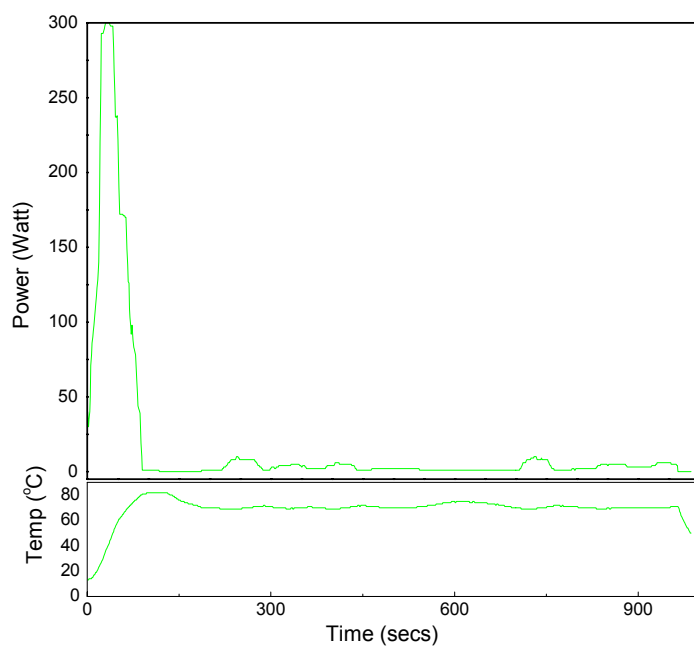


Figure 1: Power and temperature *versus* time for the polymerization of vinyl acetate mediated by EOSPE at 70°C.

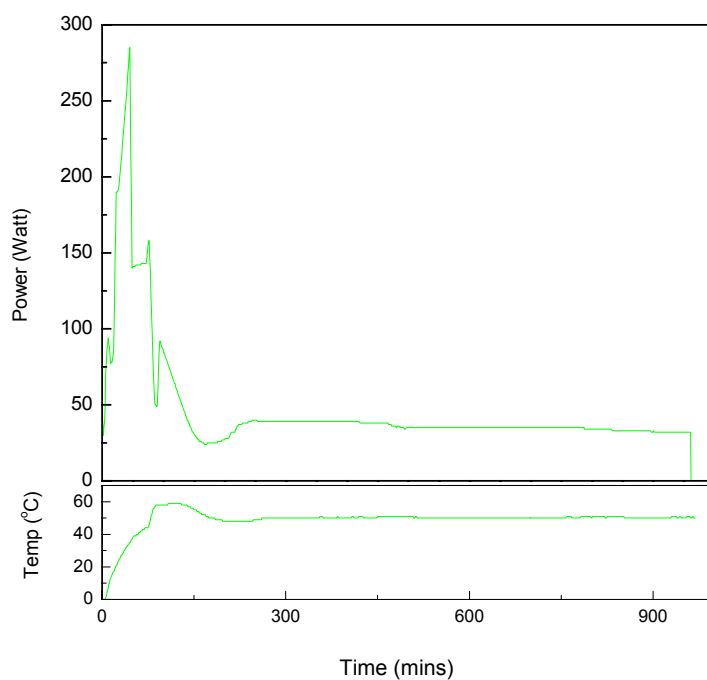


Figure 2: Power and temperature *versus* time for the polymerization of methyl acrylate mediated by ETSPE at 50°C.

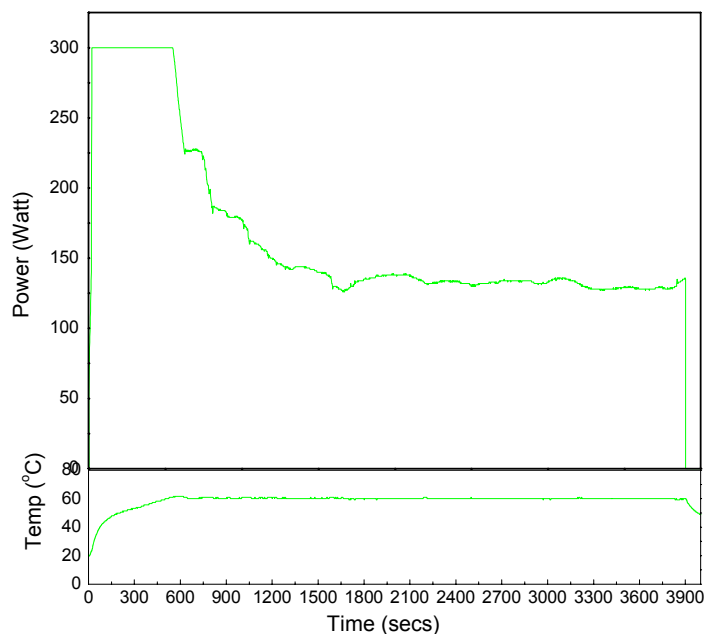


Figure 3: Power and temperature *versus* time for the polymerization of styrene mediated by CPDB at 60°C.

Analytical Conditions

CDCl_3 was added to the reaction vials to dissolve the polymer. Two decants were removed for conversion and molecular weight analysis, respectively. Polymer conversion was calculated *via* ^1H NMR on a Brüker 400 MHz spectrometer. The sample removed for molecular weight analysis was dried from the CDCl_3 and re-dissolved in THF (0.05% toluene [flow rate marker]) before analysis. Molecular weights, and molecular weight distributions, were obtained *via* Gel Permeation Chromatography (GPC) from a system equipped with a guard column, two mixed C columns (Polymer Labs) and a differential refractive index detector. Narrow molecular weight poly(styrene) (PS) standards were used as reference standards for calibration. A sample GPC trace for poly (methyl acrylate) at a monomer:RAFT:initiator ratio of 500:1:0.1, respectively, is shown in Figure 4.

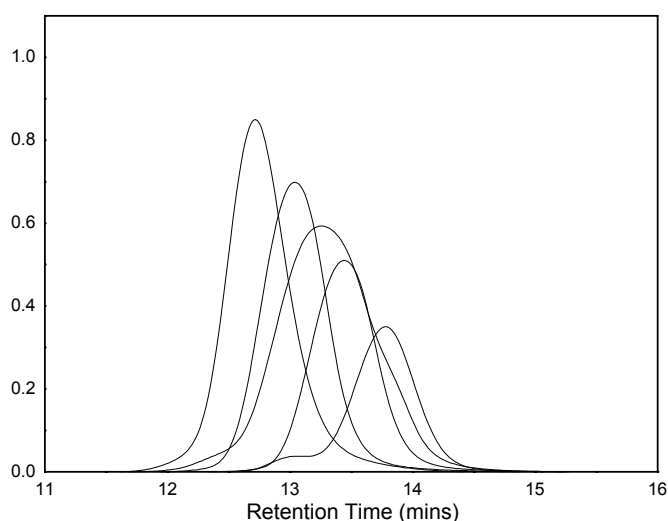


Fig.4 Evolution of molecular weight with time for the microwave induced polymerisation of methyl acrylate at 50°C

Preparation of RAFT Agents

Synthesis of ETSPE

ETSPE was prepared using the method of Wood *et al.*¹ The trithiocarbonate was purified on a silica column with hexane:diethyl ether (85:15) as a mobile phase. Percentage yield was calculated as 63 %. The purity was confirmed by ¹H and ¹³C NMR.

¹H NMR (400 MHz, CDCl₃)

δ 1.26-1.30 (*t*, 3H, SCH₂CH₃), 1.34-1.38 (*t*, 3H, OCH₂CH₃), 1.57-1.61 (*d*, 3H, SCHCH₃), 3.34-3.40 (*q*, 2H, SCH₂CH₃), 4.17-4.23 (*q*, 2H, OCH₂CH₃), 4.78-4.83 (*q*, 1H, SCHCH₃)

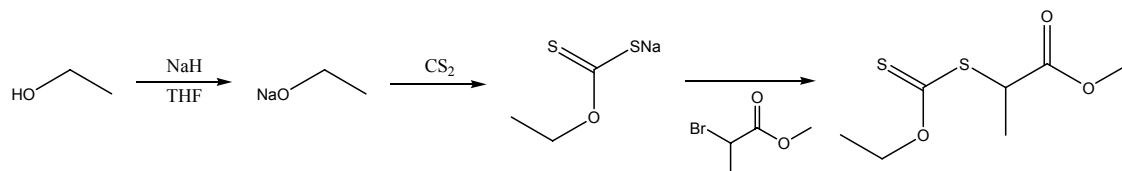
¹³C NMR (100 MHz, CDCl₃)

δ = 221.9 , 171.1 , 61.9 , 48.0 , 31.5 , 31.1 , 17.0 , 14.3 .

Synthesis of EOSPE

Sodium hydride as a 60 % dispersion in mineral oil (4.4 g, 0.11 moles) was added to a dry, 3 neck, round-bottomed flask equipped with a pressure-equalising dropping funnel, water condenser and nitrogen-filled balloon. To the sodium hydride, ethanol (50 ml) was added as a reagent, and a solvent, dropwise, over 30 minutes, under constant stirring. The contents of the flask were slowly raised to 50°C and held at this temperature for 2 hours, until all the complete evolution of H₂(g). After this time, the contents of the flask were brought to 2-3°C over ice water and carbon disulphide (15.23 g, 0.1 moles) was added drop wise to the flask over 15 minutes. The contents of the flask were then slowly raised to room temperature and held at RTP for 2 hours before being brought to 50°C to remove the excess CS₂. Methyl 2-bromopropanoate (16.7 g, 0.1 moles) was added, dropwise, over 15 mins and the contents of the flask

were allowed to reflux for 15 hours. The product was purified on a column of silica using hexane:diethyl ether (88:12) as a mobile phase. Percentage yield was calculated as 67 %.The purity was confirmed by ^1H and ^{13}C NMR.



Scheme 1: Synthetic route towards EOSPE

^1H NMR (400MHz, CDCl_3)

δ 1.17-1.21 (*t*, 3H, OCH_2CH_3), 1.31-1.34 (*t*, 3H, OCH_2CH_3), 1.47 (*d*, 3H, SCHCH_3), 4.08-4.18 (*q*, 2H, OCH_2CH_3), 4.25-4.31 (*q*, 1H, SCHCH_3) 4.51-4.55 (*q*, 2H, OCH_2CH_3).

^{13}C -NMR (100MHz, CDCl_3)

δ 212.2, 171.6, 70.2, 61.7, 47.2, 16.9, 14.3, 13.7

Synthesis of CPDB

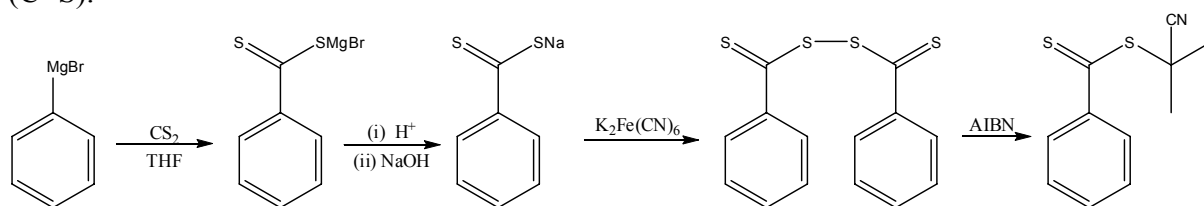
CPDB was made from a modified procedure of Moad and coworkers². Phenyl magnesium bromide (25 ml, 25 mmol), as a 1M solution in THF, was added to a flame-dried 3-neck round-bottomed flask fitted with a dropping funnel, condenser and nitrogen-filled balloon. Carbon disulphide (3.8 g, 50 mmol) was added to the THF solution at room temperature and the contents of the flask were slowly raised to 40°C and allowed to react for one hour. After this time, the contents of the flask were poured into iced water to quench any unreacted Grignard material. The magnesiumbromo dithiobenzoate was then converted to dithiobenzoic acid with conc. HCl (3.5 ml) and isolated by liquid extraction with diethyl ether (3 x 50 ml). The dithiobenzoic acid was then converted to sodium dithiobenzoate and extracted to the aqueous layer with a 2M NaOH solution (3 x 25 ml). Sodium dithiobenzoates was then reduced to S,S'-bisdithiobenzoate with potassium hexacyanoferrate (7.5 g in 75 ml of water). The $\text{K}_2\text{Fe}(\text{CN})_6$ was added dropwise to a stirred solution of the S,S'-bisdithiobenzoate over 30 minutes. The S,S'-bisdithiobenzoate was dried overnight in a vacuum oven at 45°C and added to a round-bottomed flask (3.06 g, 10 mmol) (containing ethyl acetate (50 ml) along with AIBN (2.46 g, 15 mmol). The contents of the flask were brought to reflux and held at this temperature for 18 hours. The product was purified on a silica column using hexane:ethyl acetate (9:1). Purity was confirmed by NMR.

^1H NMR (400MHz, CDCl_3)

δ 1.95 (*s*, 6H, 2x CH_3), 7.38 (*dd*, 2H, meta-ArH), 7.57 (*dd*, 1H, para-ArH) and 7.92 (*d*, 2H, ortho-ArH).

^{13}C NMR (100MHz, CDCl_3)

δ 26.5 (CH₃), 41.7 (C(CN)), 120.0 (CN), 126.6, 128.5, 132.9, 144.5 (ArC) and 227 (C=S).



Scheme 2: Synthetic route towards CPDB

References

- (1) Wood, M. R.; Duncalf, D. J.; Rannard, S. P.; Perrier, S. *Org. Lett.* **2006**, *8*, 553-556.
- (2) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993-1001.