Ambient temperature reversible addition–fragmentation chain transfer polymerisation†

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Reversible addition fragmentation chain transfer was performed at ambient temperature for the first time.

Reversible Addition Fragmentation Chain Transfer Polymerisation (the RAFT process) is a powerful technique for synthesising well-defined polymer architectures with low polydispersity.[1–3] The technique employs a transfer agent of the general formula:
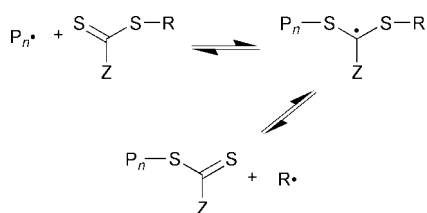
$$R-S-\underset{Z}{\overset{S}{\parallel}}$$
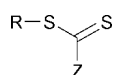
which reacts with growing polymer chains *via* Scheme 1 shown below. Reaction then proceeds with growing polymer chains reacting alternately with the two sulfur atoms in the polymeric RAFT agent. In this system, R must be a good leaving group that is able to re-initiate polymerization and the Z group strongly influences the stability of the intermediate disulfur macroradical species.[4,5]

In order to synthesise certain novel materials, it is desirable to develop a RAFT agent that can be used at rt and with initiation techniques such as UV or gamma radiation. However, preliminary studies by the authors have shown that at low temperatures (~ 25 °C), the presence of a common RAFT agent (1-phenylethyl dithiobenzoate, **1**) strongly retards the polymerisation of
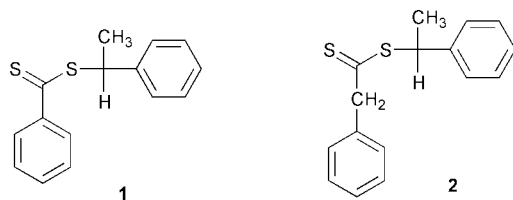
alkyl acrylates. This is consistent with previous work from the CSIRO group, which has shown that variation of the Z group from phenyl to methyl reduces retardation in the polymerization of *n*-butyl acrylate at 80 °C.[4] This retardation may be due to either a low rate of fragmentation of the intermediate (lessening the number of propagating radicals), or failure of the phenyl-

ethyl group to re-initiate polymerization at these low temperatures. To counter the first problem, a simple variation was made to the Z group of the RAFT agent, in order to give a less stable macroradical intermediate, thereby increasing the rate of fragmentation. In this study, by changing the Z group from a phenyl to a benzyl group, the radical in the RAFT intermediate is changed from being in a disulfur benzylic position to a less stable disulfur alkyl position. This should increase the rate of fragmentation and result in faster establishment of the RAFT equilibrium. Therefore, using such a RAFT agent it could be anticipated to observe living behaviour in the polymerization of alkyl acrylates at lower temperatures, rather than the demonstrated retardation caused by 1-phenylethyl dithiobenzoate. The RAFT agent synthesised for this study was 1-phenylethyl phenyldithioacetate (**2**).‡

Methyl acrylate was polymerised in septa capped ampoules in a water bath at rt using AIBN as the initiator and 1-phenylethyl phenyldithioacetate (1-PEPDTA) as the RAFT agent. Given that AIBN has a much longer half-life at 25 °C than it does at 60 °C, a higher than normal concentration was used (36.1×10^{-3} mol L^{-1}). A significant exotherm was observed in the control experiments (methyl acrylate, AIBN only), with the resultant runaway reaction causing the monomer to boil and the septa to break in the first ten minutes of the reaction. Conversely, the polymerization of methyl acrylate with added 1-PEPDTA proceeded without autoacceleration *via* pseudo first order kinetics, as shown in Fig. 1.§

Further, use of 1-PEPDTA in polymerisation of methyl acrylate at 25 °C gives low polydispersity poly(methyl acrylate) (M_n = 241,417, PDI = 1.19) that shows living behaviour (*i.e.* the molecular weight increases linearly with conversion). This is demonstrated in Fig. 2.

It should be noted that the molecular weights obtained experimentally adhere closely to those predicted from theory (Fig. 2, unbroken line). The exception to this is the final data point, where the theoretical molecular weight is considerably lower than the experimental one. An explanation for this deviation is the use of Mark Houwink Sakurada coefficients for
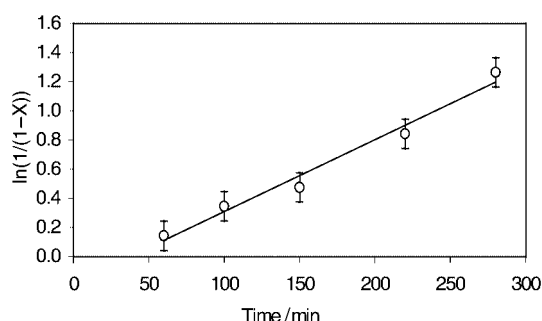
Scheme 1

Fig. 1 Pseudo first order rate plot for the bulk polymerisation of methyl acrylate mediated with 1-PEPDTA at 25 °C. Error determined from duplicates.

† Electronic supplementary information (ESI) available: data used for the graphs in Figs. 1 and 2. See http://www.rsc.org/suppdata/cc/b1/b101794m/
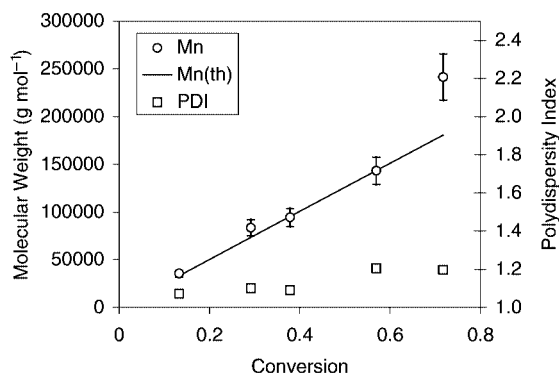
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Fig. 2 Evolution of molecular weight and polydispersity index with conversion for 1-PEPDTA mediated polymerisation of methyl acrylate at 25 °C.

polystyrene in the molecular weight determination of the polymer. When analysing a polyacrylate, this would be expected to give an error anywhere between 10 and 100% (with larger error at higher molecular weight), and therefore may account for the observed discrepancy between the actual and theoretical values.

These results demonstrate that by adjusting the structure of the Z group in the RAFT agent living polymerization at rt is possible. The structural adjustment is required to decrease the stability of the intermediate radical, therefore causing the equilibrium (Scheme 1) to shift to increase the concentration of propagating polymer chains. In this study this was achieved by changing the RAFT agent from 1-phenylethyl dithiobenzoate, which gives rise to a disulfur benzylic radical intermediate, to 1-phenylethyl phenyldithioacetate, which yields a less stable disulfur alkyl radical intermediate.

Notes and references

‡ *Synthesis*: 1-Phenylethyl phenyldithioacetate was synthesised using the following method. Benzyl chloride (20 g) was added dropwise to a mixture of magnesium turnings (3.75 g) in dry diethyl ether (100 ml). Following the vigorous initial reaction, the solution was refluxed for 3 h to ensure complete reaction. The mixture was then chilled and carbon disulfide (12.0 g) was added dropwise over 30 min, and then the mixture stirred at 0 °C for the following 2 h. The mixture was then poured onto ice-water (300 ml) and the aqueous portion collected following three washes with diethyl ether. A final layer of diethyl ether was added, and the mixture acidified using 30% aqueous HCl. Phenyldithioacetic acid (~ 7 g) was collected *via* rotary evaporation of the ether. The acid was then reacted with styrene (9.0 g), with a small amount of acid catalyst (toluene-*p*-sulfonic acid) in CCl$_4$ (10 g). The product was then precipitated in cold methanol and recrystallised from methanol as fine yellow crystals (3.2 g). ^{1}H NMR: δ = 1.7 d 3H, δ = 4.2 s 2H, δ = 5.1 q 1H, δ = 7.3 m 10H. ^{13}C NMR (CDCl$_3$): 20.5, 49.9, 57.9, 127.2, 127.6, 127.7, 128.5, 128.6, 129.1, 136.9, 141.0 and 233.6. IR: Aromatic C–H stretch, 3062, 3028 cm^{-1}; Aliphatic C–H stretch, 2966, 2925 cm^{-1}; Overtone indicative of monosubstituted aromatic 2000–1650 cm^{-1}; Aromatic ring stretch, 1601, 1494, 1453 cm^{-1}; Thiocarbonyl C=S stretch, 1219, 1125, 1028 cm^{-1}; Out of plane aromatic C–H bend 764, 697 cm^{-1}; Weak sulfide C–S stretch, 646, 591 cm^{-1}. Melting point = 35 °C.

§ *Polymerization*: A solution of methyl acrylate with an initial 1-PEPDTA concentration of 3.9 × 10^{-3} mol L^{-1} and an AIBN concentration of 36.1 × 10^{-3} mol L^{-1} was prepared. The stock solution was divided into five individual ampoules and deoxygenated by purging with nitrogen for approximately 15 min. The ampoules were then placed in a constant temperature water bath at 25 °C, and an ampoule was removed after 60, 100, 150, 220 and 280 min. The reactions were stopped by cooling the solutions in an ice bath followed by the addition of hydroquinone. The polymer was isolated by evaporating off the residual methyl acrylate, initially in a fume cupboard to remove the bulk of the liquid, and then in a vacuum oven at 25 °C. Final conversions were measured by gravimetry, and the molecular weight distribution measured using gel permeation chromatography. Each experiment was performed in duplicate. Blank solutions, containing only methyl acrylate and AIBN were also prepared and polymerised using the same methods.

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