Observations on Reversible Addition Fragmentation Chain Transfer (RAFT) / Polymerisations in Solution and Emulsion

Graham Street, *Dr D Illsley[b], Dr S J Holder[a]*

Functional Materials Group, School of Physical Sciences, University of Kent[a]. Sun Chemical, St Mary Cray Research. Center, St Mary Cray[b].

In recent years controlled radical polymerisation techniques have been developed whereby the termination reactions found in normal free radical polymerisation can be suppressed[1]. One such technique is reversible addition fragmentation chain transfer (RAFT) polymerisation. The mechanism of RAFT polymerisations involves a reversible addition-fragmentation sequence in which the transfer of the S=C(Z)S moiety (where Z represents a side group responsible for modifying the reactivity of the dithio carbonyl portion toward free radical addition) between active and dormant chains serves to maintain the living character of the polymerisation[2] (Scheme 1).

The success of the RAFT agent in providing living character is attributed to the rapid rate of exchange between dormant and living chains[3].
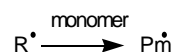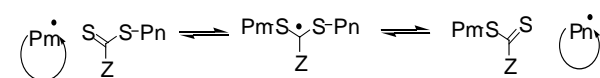
Initiation
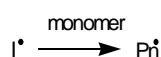
Chain transfer
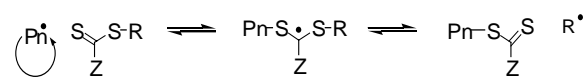
Reinitiation

Chain equilibration

Scheme 1:mechanism of RAFT polymerisation

Solution polymerisations

The RAFT agent PPPDTA (figure 1) has been synthesised and used in the successful polymerisation of several monomers.
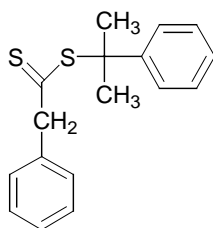

Figure 1: RAFT agent 2-phenylprop-2-yl phenyl dithio acetate

The kinetics of these polymerisations at various temperatures has been investigated, with 60°C being found to be the optimum (figure2).
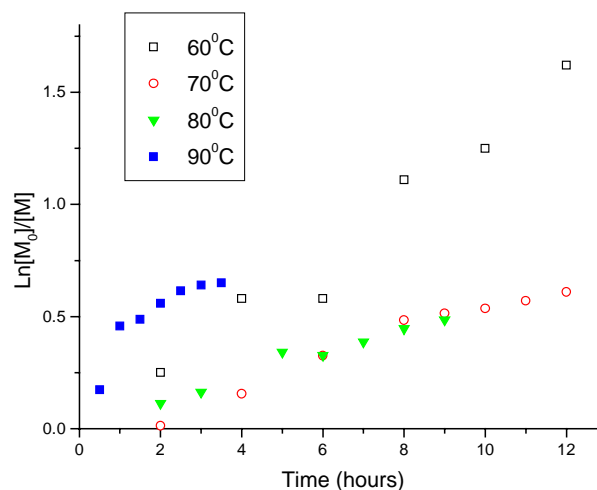

Figure 2: Kinetic data from PPPDTA mediated polymerisation of MMA at various temperatures

NMR data from polymerisations at higher temperatures showed possible evidence of RAFT agent degradation leading to non first order kinetics at 90°C. A short chain (Dp =20) PMMA sample with the teminal thiobenzyl group was heated in Xylene at 90°C in the presence of AIBN. The signal from the benzyl CH_2 protons disappears showing possible degradation of the RAFT agent.
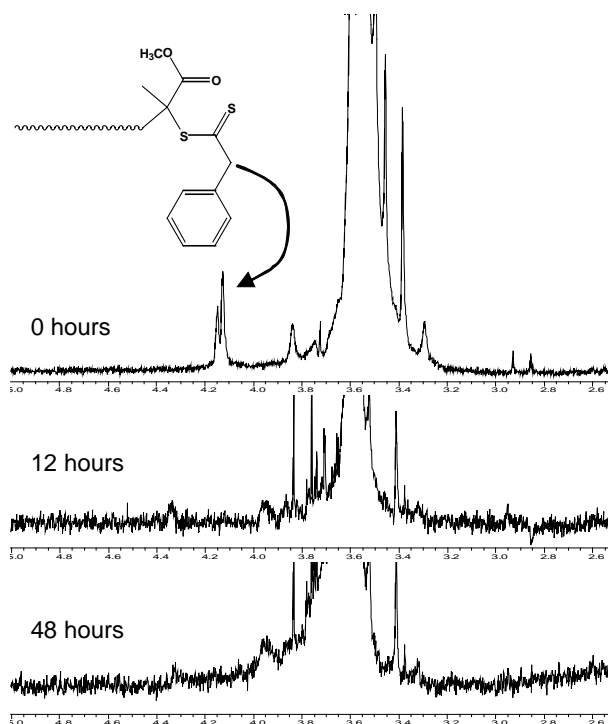

Figure 3:1H NMR spectra showing the possible degradation of terminal thiobenzyl group

Table 1: Experimental data for the synthesis of homo polymers mediated by PPPDTA

Monomer	Dp theory [a]	Dp SEC [b]	PDI	Yield %
MMA	200	221	1.19	80%
BMA	200	235	1.23	80%
PS	200	230	1.19	60%
OEGMA	25	21	1.20	75%

a mol monomer /mol RAFT agent
b GPC calibrated with PMMA standards

Polymers synthesised at 60°C were used as polymeric RAFT agents in chain extension reactions to yield block copolymers (Table 2). Good control over molecular weights and low polydispersity (<1.4) showed that the reactions proceeded with 'living' character.

Table 2: Experimental data for the synthesis of block co-polymers by chain extension of macro RAFT agents

Macro RAFT	Monomer	Dp theory [a]	Dp SEC [b]	PDI
PMMA	PBMA	1000	1118	1.41
PMMA	PS	1000	1500	1.27
PBMA	PMMA	250	300	1.40
PS	PMMA	250	275	1.16
POEGMA	PODA	100	40	1.27

a mol monomer /mol RAFT agent
b GPC calibrated with PMMA standards

Emulsion polymerisations

Other groups using styrene seeds have achieved incorporation of the RAFT agent in seeded emulsion polymerisations (figure 4)[3]. The use of a polymethyl methacrylate seed has so far been unreported in the literature. We report here the successful use of a polymethyl methacrylate seed to control the emulsion polymerisation of methyl methacrylate. Yielding polymers of controlled molecular weight and narrow polydispersity (<1.5) (Table 3) however reproducibility of these initial results has proved difficult.
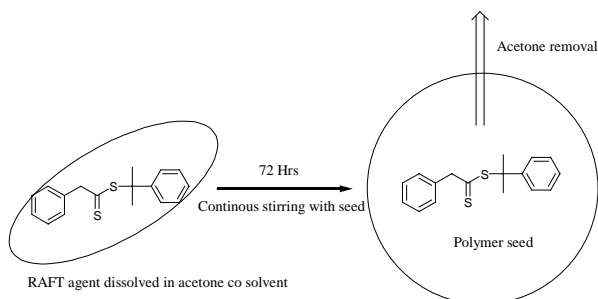

Figure 4: Acetone transport technique[3]

Table 3: Experimental data from PPPDTA mediated seeded emulsion polymerisation

Monomer	Dp theory [a]	Dp SEC [b]	PDI	Yield %
PMMA	200	182	1.43	50%
PMMA	500	442	1.32	60%

a mol monomer /mol RAFT agent
b GPC calibrated with PMMA standards

References:
1: Matyjaszewski K, Xia J H, Chem review 101 (9): 2921-2990 *2001*
2: Chong (Bill) Y K, Krstina J, Jeffery J, Le T P T, Postma A, Rizzardo E, Thang S H Macromolecules 36 2256 *2003*
3:Chiefari J, Chong (Bill) Y K Ercole F, Krstina J, Jeffery J, Le T P T, Mayadunne R T A, Meijs G F, Moad C L, Moad G, Rizzardo E, Thang S H Macromolecules 31 5559 *1998*
4:Prescott S W, Ballard M J, Rizzardo E, Gilbert R G Macromolecules 35 5417 *2002*