

Living free radical polymerization with reversible addition – fragmentation chain transfer (the life of RAFT)

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Abstract: Free radical polymerization with reversible addition–fragmentation chain transfer (RAFT polymerization) is discussed with a view to answering the following questions: (a) How living is RAFT polymerization? (b) What controls the activity of thiocarbonylthio compounds in RAFT polymerization? (c) How do rates of polymerization differ from those of conventional radical polymerization? (d) Can RAFT agents be used in emulsion polymerization? Retardation, observed when high concentrations of certain RAFT agents are used and in the early stages of emulsion polymerization, and how to overcome it by appropriate choice of reaction conditions, are considered in detail. Examples of the use of thiocarbonylthio RAFT agents in emulsion and miniemulsion polymerization are provided.

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INTRODUCTION

In recent years, considerable effort^{1,2} has been expended to develop free radical processes that display the characteristics of living polymerization. Ideally, these polymerizations provide molecular weights that are predetermined by reagent concentrations and conversion, make very narrow polydispersities possible, and, most importantly, give polymer products that can be reactivated for chain extension or block synthesis.

Recently we have described a new method for conferring living character on a free radical polymerization.^{3–10} The process involves conducting a polymerization in the presence of a reagent (1) which reacts by reversible addition–fragmentation chain transfer (see Scheme 1). Accordingly, we designated the method RAFT polymerization and the reagents used (1), RAFT agents.⁵ We have shown that the process is applicable to a wide range of monomers (most monomers polymerizable by free radical methods) and reaction conditions. The effectiveness of the reagents 1 depends on their transfer constant, which is determined by the nature of the groups X, Z and R. The most effective reagents for RAFT polymerization are certain thiocarbonylthio compounds 2, where X is sulfur, R is a free radical leaving-group that is capable of reinitiating polymerization and Z is a group that modifies the activity of the RAFT agent.^{5,6} Macromonomers 3, where X is CH₂ can also function as RAFT agents.^{3,4,11,12}

This paper will discuss some of the advantages and limitations of RAFT polymerization using thio-

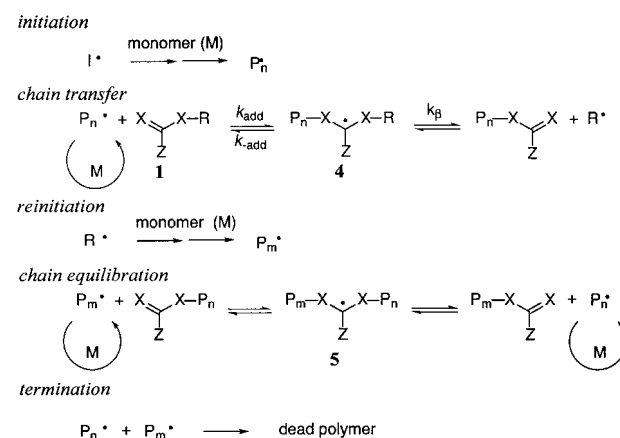
carbonylthio compounds 2 by addressing the following issues:

- How living is RAFT polymerization?
- What factors control the activity of thiocarbonylthio compounds in RAFT polymerization?
- How do rates of polymerization differ from those of conventional radical polymerization?
- Can RAFT agents be used in emulsion polymerization?

RESULTS AND DISCUSSION

How living is RAFT polymerization?

The polymers formed by RAFT polymerization can be



Scheme 1. Mechanism of RAFT polymerization.

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reactivated for chain extension or for use as precursors to produce blocks, stars or polymers of more complex architectures.⁶ The active functionality, the thiocarbonylthio group(s), are retained (in the case of low molecular weight polymers, the end-groups have been determined by NMR or mass spectrometry).^{5,6} Polymers of narrow polydispersity (<1.2) can be formed.^{5,6} Thus, RAFT polymerization meets most of the established criteria for living polymerization.^{13,14} However, RAFT polymerization involves free radical intermediates. Thus, some radical-radical termination, a complication in all forms of living radical polymerization, cannot be avoided, and an amount of dead polymer, determined by the number of chains initiated by initiator-derived radicals, must ultimately be formed.

To achieve the narrowest polydispersities and obtain the highest degree of livingness in RAFT polymerization, it is clearly desirable to minimize the initiator concentration or, more accurately, the number of initiator-derived chains. Notwithstanding this requirement, one of the major benefits of the RAFT process, over other forms of living radical polymerization, is that the reaction conditions usually employed are typical of those used for conventional free radical polymerization.²

The results for a series of thermal styrene polymerizations performed with a range of concentration of cumyl dithiobenzoate (**2a**) are shown in Fig 1. The polystyrene formed with the highest concentration of the RAFT agent appears to be of very narrow polydispersity and has a unimodal molecular weight distribution (see Fig 1). The conversion (about 55%) is slightly reduced with respect to the control experiment (about 72%). This may be the result of a reduced gel or Trommsdorf effect. As the concentration of RAFT agent used in the experiments was decreased, polydispersities were observed to increase and a high molecular weight shoulder appeared in the molecular weight distribution (Fig. 1). It is notable that the peak molecular weight of the shoulder is about twofold higher than the molecular weight of the main peak. This is consistent with the shoulder arising from termination by coupling of polystyryl propagating radicals. For lower dithioester concentration the molecular weight distribution is also seen to tail to lower molecular weights.

The extent of radical-radical termination in RAFT polymerization is most clearly evident during the synthesis of star polymers. The four-armed star polymers (**7**) were prepared using the tetrafunctional trithiocarbonate (**6**) as precursor (Scheme 2). The mode of star growth depends on the structure of the precursor.

Benzylic radicals are substantially better leaving-groups than primary alkyl radicals. Thus, for the example shown in Scheme 2 the star is dormant. All propagating radicals are linear (not attached to the star) and of lower (about fourfold) molecular weight. Dead chains formed by radical-radical reaction are therefore also linear and of two- or fourfold lower

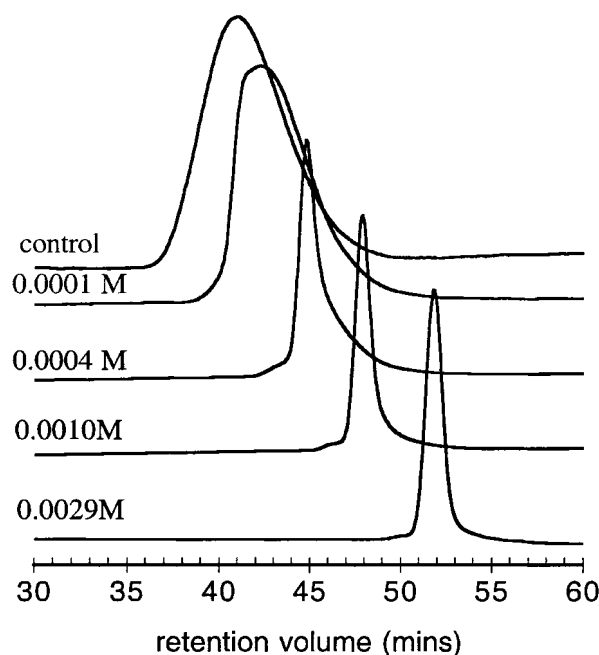
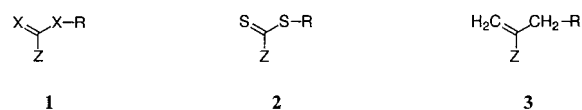
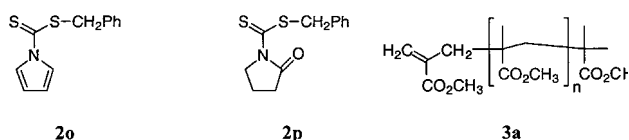


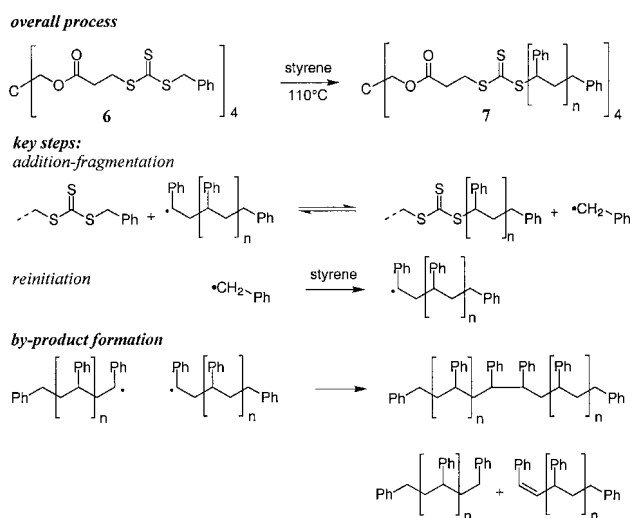
Figure 1. GPC elution profiles for polystyrenes prepared by thermal polymerization of styrene in the presence various concentrations of cumyl dithiobenzoate (**2a**) at 110°C for 16h. From top to bottom are the control (\bar{M}_n 323700 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.74, 72% conversion), 0.0001 M **2a** (\bar{M}_n 189300 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.59, 59% conversion), 0.0004 M **2a** (\bar{M}_n 106600 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.21, 60% conversion), 0.0010 M **2a** (\bar{M}_n 48065 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.07, 55% conversion), 0.0029 M **2a** (\bar{M}_n 14400 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.04, 55% conversion).

molecular weight than the star, depending on whether termination is by combination or disproportionation. Gel permeation chromatography (GPC) with refractive index (RI) detection for the polymer formed shows the development of a small peak that may be attributed to the termination product (see Fig. 2). The moles of dead polymer will be approximately equal to half the moles of initiating radicals generated by thermal initiation (assuming termination is predominantly by combination). Notwithstanding this, the overall polydispersity remains narrow (1.22 at 96% conversion).



- | | |
|---|--|
| 2a R= C(CH ₃) ₂ Ph, Z=Ph | 2h R= CH ₂ Ph, Z=CH ₃ |
| 2b R=CH(CH ₃)Ph, Z=Ph | 2i R= CH ₂ Ph, Z=SCH ₂ Ph |
| 2c R= CH ₂ Ph, Z=Ph | 2j R=CH ₂ Ph, Z=OPh |
| 2d R= C(CH ₃) ₂ CN, Z=Ph | 2k R=CH ₂ Ph, Z=OC ₆ F ₅ |
| 2e R= C(CH ₃) ₂ CO ₂ Et, Z=Ph | 2l R=CH ₂ Ph, Z=OC ₂ H ₅ |
| 2f R= C(CH ₃) ₃ , Z=Ph | 2m R=CH(CH ₃)Ph, Z=OEt |
| 2g R= C(CH ₃) ₂ CH ₂ C(CH ₃) ₃ , Z=Ph | 2n R=CH ₂ Ph, Z=NEt ₂ |





Scheme 2. Key reaction pathways involved in *star*-polystyrene synthesis.

The polydispersity of the star is 1.08. Analysis of the star by GPC with ultraviolet (UV) detection at 310nm shows the main peak to be unimodal (ie, the small peak observed in the RI trace is absent), confirming that the small peak is due to dead polymer which does not contain the trithiocarbonate chromophore.

These examples show that dead chains are formed by radical-radical termination during RAFT polymerization. The amount of such dead chains formed is controlled by the number of chains initiated. The fraction of dead chains formed in RAFT polymerization can be estimated by comparing the number of moles of polymer formed to the moles of thiocarbonylthio compound employed

$$[\text{Polymer formed}] = \frac{[M]_t - [M]_o}{\bar{X}_n}$$

where $[M]_t - [M]_o$ is the monomer consumed and \bar{X}_n is the degree of polymerization.

Another method which can provide a rough guide to the selection of reaction conditions is to compare the molecular weight of a polymer formed under similar conditions in the absence of the RAFT agent. Assuming similar conversions, a tenfold lower molecular weight for the polymer formed in the presence of RAFT agent will usually ensure that the fraction of dead chains is less than 10%.

What controls the activity of thiocarbonylthio compounds?

Chain transfer in RAFT polymerization involves addition and fragmentation steps as shown in Scheme 1. The formation of the intermediate (4 and/or 5) has recently been confirmed by ESR spectroscopy.¹⁵ As for conventional chain transfer, the chain transfer constant (C_{tr}) is given by the ratio of the rate constant for chain transfer to that for propagation (k_{tr}/k_p). However, in the case of reagents that react by addition

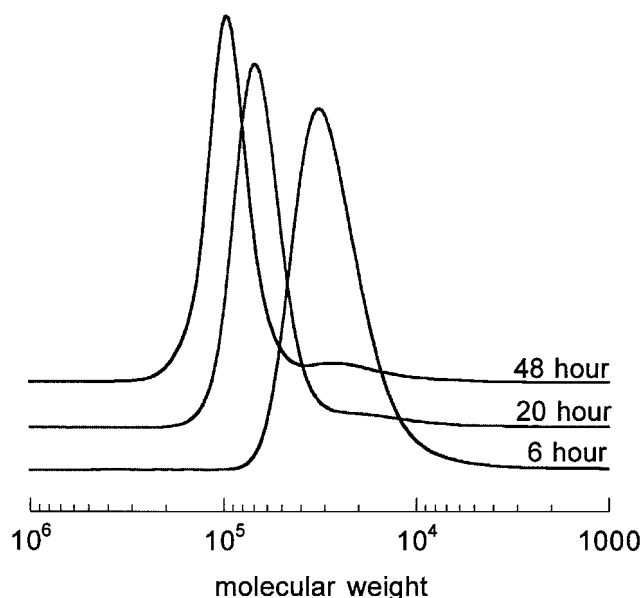


Figure 2. GPC traces for *star*-polystyrene **7** formed by polymerization of styrene (bulk) with tetrakis(trithiocarbonate) **6** 0.0073M for 6h (\bar{M}_n 25600 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.18, 25% conversion), 20h (\bar{M}_n 56600 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.17 (main peak has \bar{M}_n 63900 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.07), 63% conversion), and 48h (\bar{M}_n 76300 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.22 (main peak has \bar{M}_n 92000 g mol⁻¹, \bar{M}_w/\bar{M}_n 1.08), 96% conversion).

fragmentation, k_{tr} is a composite term which depends on the rate constant for addition to the thiocarbonyl group k_{add} and the partitioning of the intermediate formed (4) between starting materials and products as shown in eqn (1)¹¹

$$k_{tr} = k_{add} \frac{k_{\beta}}{k_{-add} + k_{\beta}} \quad (1)$$

The transfer constants of various thiocarbonylthio compounds have been found to span more than five orders of magnitude (<0.01 to >1000) depending on the groups Z and R and the particular monomer(s) being polymerized.¹⁶⁻¹⁸ Theory suggests that to yield narrow polydispersities (<1.5) in a batch polymerization with degenerative chain transfer, the transfer constant of the RAFT agents should be greater than two.^{2,19,20} The use of feed polymerization allows synthesis of narrow polydispersity polymers from less active agents.^{4,12} Note that in designing reaction conditions, it is necessary to consider the transfer constants of both the initial RAFT agent and that of the polymeric RAFT agents formed during the course of the polymerization.

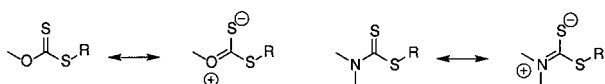
To assess the affect of the Z group on the activity of thiocarbonylthio compounds in RAFT polymerization, the transfer constants of a series of benzyl thiocarbonylthio compounds of general structure $Z-C(=S)SCH_2Ph$ in styrene polymerization have been measured (see Table 1). This involved following the relative rates of consumption of transfer agent and monomer.¹⁸ Because the leaving group R (and the propagating species) are common, differences in transfer constants can be largely attributed to differ-

Table 1. Apparent transfer constants (C_{tr}) for benzyl thiocarbonylthio compounds $Z-C(=S)SCH_2Ph$ in styrene polymerization at 110°C¹⁸

RAFT agent	C_{tr}	RAFT agent	C_{tr}
2c , Z = Ph	26 ^a	2k , Z = OC ₆ F ₅	2.3
2i , Z = SCH ₂ Ph	18 ^a	2p , Z = lactam	1.6
2h , Z = CH ₃	10 ^a	2j , Z = OPh	0.72
2o , Z = pyrrole	9 ^a	2n , Z = NEt ₂	0.01 ^b

^a In the case of the more active reagents, the measured 'transfer constants', obtained from the slope of a plot of \log [RAFT agent] vs \log [monomer], are dependent on the initial concentration of RAFT agent and decrease with increasing concentration of the RAFT agent. The phenomenon is explicable in terms of the reversibility of the transfer reaction and values quoted (for [RAFT agent] = 0.03 M and bulk monomer) should be regarded as minimum values.

^b 80°C.

**Scheme 3.** Canonical forms of xanthates and dithiocarbamates.

ences in the reactivity of the C=S double bond. This hypothesis is supported by the observation that the trend in activity follows trends in the heats of reaction for C=S addition or in LUMO energies.¹⁸ The transfer constants decrease in the series where Z is aryl > alkyl \approx alkylthio \approx pyrrole > aryloxy > amido > alkoxy > dialkylamino. The low activity of xanthates and dithiocarbamate derivatives can be qualitatively understood in terms of the importance of zwitterionic canonical forms (see Scheme 3) which serve to reduce the C=S double bond character and raise the LUMO (and HOMO) energy.^{10,18}

R should be a good free radical leaving-group both in absolute terms and relative to the propagating species derived from the monomer being polymerized. The effect of the R group on activity was gauged by determining the apparent transfer constants of a series of dithiobenzoate derivatives of general structure PhC(=S)S-R in methyl methacrylate polymerization (Table 2).¹⁷ Based on the reasonable assumption that the R group does not dramatically effect the rate of addition to the thiocarbonyl group, the magnitudes of

the transfer constants should reflect the partitioning of the intermediate between starting materials and products and relative leaving group ability. The comparatively low transfer constants of benzyl and 1-phenylethyl dithiobenzoates indicate that steric factors may be more important than radical stability in determining leaving-group ability. The importance of steric factors is also indicated by the finding that 2,4,4-trimethylpent-2-yl dithiobenzoate (**2g**) has a much higher transfer constant than *tert*-butyl dithiobenzoate (**2f**). The finding that cyanoisopropyl dithiobenzoate (**2d**) appears to have a higher transfer constant than cumyl dithiobenzoate (**2a**) may suggest that polar factors are also important in determining the transfer constant. However, the 'transfer constants' for the more active compounds, which are measured by comparing the rate of consumption of RAFT agent as a function of conversion, decrease with the concentration of the RAFT agent.¹⁷ It should be noted that for the RAFT agent to be effective, R', besides being a good homolytic leaving group with respect to the propagating radical, must also be efficient in reinitiating polymerization.

How do rates of polymerization differ from those of conventional radical polymerization?

Many RAFT agents behave as ideal chain-transfer agents and rates of polymerization are similar (within $\pm 20\%$) to those of similar polymerizations carried out in the absence of RAFT agents. However, it has been found that significant retardation may result in some circumstances.

One of the more versatile RAFT agents is cumyl dithiobenzoate (**2a**).⁵ However, retardation (and an apparently low transfer constant) has been observed when this reagent is used either in high concentrations to form low molecular weight polymers or during the early stages of emulsion polymerization (see below). Based on the mechanism shown in Scheme 1, several explanations for retardation may be envisaged. These include the following:

- Slow fragmentation of the adduct (**4**) formed from the initial RAFT agent (**1**).
- Slow fragmentation of adduct (**5**) formed from the polymeric RAFT agent.
- Slow reinitiation by the expelled radical (R').

Table 2. Apparent transfer constants (C_{tr}) for dithiobenzoate derivatives PhC(=S)S-R in methyl methacrylate polymerization at 60°C.¹⁷

RAFT agent	C_{tr}	RAFT agent	C_{tr}
2d , R = C(CH ₃) ₂ CN	13 ^a	2g , R = C(CH ₃) ₂ CH ₂ C(CH ₃) ₃	0.4
2a , R = C(CH ₃) ₂ Ph	10 ^a	2b , R = CH(CH ₃)Ph	0.16
2e , R = C(CH ₃) ₂ CO ₂ Et	2	2f , R = C(CH ₃) ₃	0.03
		2c , R = CH ₂ Ph	0.03

^a In the case of the more active reagents, the measured 'transfer constants', obtained from the slope of a plot of \log [RAFT agent] vs \log [monomer], are dependent on the initial concentration of RAFT agent and decrease with increasing concentrations of the RAFT agent. The phenomenon is explicable in terms of the reversibility of the transfer reaction and values quoted (for [RAFT agent] = 0.03 M and bulk monomer) should be regarded as minimum values.

Table 3. Molecular weight and conversion data for styrene polymerizations in toluene (50% w/w) at 110 °C in the presence of various dithioesters^a

RAFT agent	[RAFT agent] (M)	Time (min)	\bar{M}_n (g mol ⁻¹)	\bar{M}_w/\bar{M}_n	Conversion (%)
2a	0.018	60	2010	1.07	1
2a	0.018	120	3250	1.07	17
2a	0.003	60	19200	1.23	15
2d	0.022	60	2330	1.08	15
2d	0.022	120	4100	1.07	27
–	0	60	61900	1.57	21
–	0	120	68500	1.62	28

Table 4. Molecular weight and conversion data for *n*-butyl acrylate polymerizations in MEK (50% w/w) at 80 °C in the presence of various dithioesters^a

RAFT agent	[RAFT agent] (M)	Time (min)	\bar{M}_n	\bar{M}_w/\bar{M}_n	Conversion (%)
2a	0.023	60	275	1.11	2
2a	0.023	120	555	1.20	4
2a	0.003	60	34000	1.25	32
2c	0.025	60	790	1.16	3
2c	0.025	120	1400	1.21	7
2h	0.034	60	3550	1.18	25
2h	0.034	120	6100	1.17	50
–	0	60	76050	2.63	68
–	0	120	89350	2.34	81

^a Initiator azobis(methyl isobutyrate) 0.001 M.

- (d) Specificity for the expelled radical (R[•]) to add to the RAFT agent rather than to monomer.
 (e) Specificity for the propagating radical (P_n[•]) to add to the RAFT agent rather than monomer (ie transfer constant too high!).

Conversion and molecular weight data for styrene and *n*-butyl acrylate polymerizations carried out in the presence of various dithioesters, including cumyl dithiobenzoate (**2a**), are shown in Tables 3 and 4, respectively.

In the case of styrene polymerization in the presence of cumyl dithiobenzoate (**2a**), retardation is manifest as an inhibition period lasting up to 1 h during which the RAFT agent is only slowly consumed (see Table 3). The molecular weight is significantly greater than that expected based on complete consumption of the RAFT agent during this period. For longer reaction times, when the initial RAFT agent is converted to a polymeric species, the polymerization rate increases. Because cumyl radical is anticipated to be a good free radical leaving-group, the problem is attributed to the cumyl radical being relatively slow to initiate styrene polymerization (ie (c) or (d) above). The use of a RAFT agent (**2d**) containing a more effective initiating species (the cyanoisopropyl radical) alleviated retardation (see Table 3).

Polymerizations of *n*-butyl acrylate performed with cumyl (**2a**) or benzyl dithiobenzoates (**2c**) as the RAFT agent are also markedly retarded. Molecular weights are very low, which is consistent with complete consumption of the initial RAFT agent (see Table 4). Retardation is therefore associated with the polymeric RAFT agent and with slow fragmentation of the intermediate (**5**) (ie (b) or (e) above). Consistent with

this hypothesis, retardation was alleviated by use of a less active RAFT agent, benzyl dithioacetate (**2h**). It is anticipated that RAFT agents with lower transfer constants should also provide faster fragmentation rates.

Can RAFT agents be used in emulsion polymerization?

We have previously reported that RAFT polymerization with methacrylate macromonomers (**3a**)^{3,4} or thiocarbonylthio compounds (**2**)^{5,7} as the RAFT agent can be successfully used to form block copolymers and narrow polydispersity homopolymers under emulsion polymerization conditions. To achieve narrow polydispersities and acceptable polymerization rates, it is necessary to pay particular attention to the choice of RAFT agent and the polymerization conditions.

Emulsion polymerization of styrene has been performed with five RAFT agents using similar reaction conditions (Table 5). Polymerization rates were generally very fast, with instantaneous conversions typically in the range 90–99%. Best results were

Table 5. Molecular weight and conversion data obtained in emulsion polymerizations of styrene at 80 °C in the presence of various RAFT agents^a

RAFT agent	\bar{M}_n (g mol ⁻¹)	\bar{M}_w/\bar{M}_n	Conversion (%)
2a	39850	7.09	96
2c	53210	1.37	>99
2h	35580	1.38	>99
2l	32370	1.98	>99
2m	31300	2.04	>99
–	132600	2.71	>99

^a For experimental conditions and reagent concentrations see Experimental.

Table 6. Molecular weight and conversion obtained during synthesis of poly(methyl methacrylate)-*block*-polystyrene by emulsion polymerization in the presence of benzyl dithioacetate (**2h**)^a

Temperature (°C)	Time (min)	Monomer added (ml)		\bar{M}_n^b (g mol ⁻¹)	\bar{M}_w/\bar{M}_n	Conversion (%) ^c
		Styrene	MMA			
80	30	6	0	7700	1.37	43
80	60	12	0	22000	1.33	89
80	75	15	0	23700	1.35	>99
90	100	15	7.5	34600	1.41	92
90	130	15	15	39000	1.56	84
90	190	15	15	41300	1.57	87

^a For experimental conditions and reagent concentrations see Experimental.

^b GPC molecular weight in polystyrene equivalents.

^c Conversion of total monomers added.

obtained with benzyl dithiobenzoate (**2c**) and benzyl dithioacetate (**2h**) (polydispersities <1.4). The xanthate esters gave molecular weight control but relatively broad polydispersities (2.0). The broader polydispersity may be attributed to the low transfer constant of these reagents (see below). The failure of cumyl dithiobenzoate (**2a**) to give a narrow polydispersity product is attributed to marked retardation observed in the early stages of polymerization. It was also clear that this reagent was not uniformly dispersed in the polymerization medium during this time.

Poly(methyl methacrylate)-*block*-polystyrene was prepared by 'one pot' procedures involving sequential addition of the monomers (see Table 6). In the first experiment, the polystyrene block was prepared first using benzyl dithioacetate (**2h**) as the RAFT agent. On adding MMA, molecular weights continued to increase linearly with monomer consumed (see Fig 3) though some broadening of the molecular weight distribution was observed. GPC with UV detection (270 nm; PMMA is transparent at this wavelength) shows that the polystyrene first block is fully incorpo-

rated into the block copolymer (see Fig. 4). It is notable that previous attempts to prepare poly(methyl methacrylate)-*block*-polystyrene by batch polymerization in bulk have been unsuccessful. That result was attributed to the low transfer constant of polystyryl RAFT agents in MMA polymerization.¹⁷ Success in this case is attributed to the use of a feed addition protocol in which the instantaneous concentration of monomer is maintained at a low level.

In the second experiment, a first block of poly(methyl methacrylate) was prepared with cumyl dithiobenzoate (**2a**) as the RAFT agent (see Table 7). To minimize retardation, cumyl dithiobenzoate and monomer were added together during the very early stages of the reaction (corresponding to 10 min reaction time). This step produces low molecular weight poly(methyl methacrylate) RAFT agent. Again, a linear increase in molecular weight with monomer consumed was observed (see Fig 5). However, polydispersities obtained were broad compared to that obtained in similar experiments carried out with a methyl methacrylate macromonomer (**3a**)

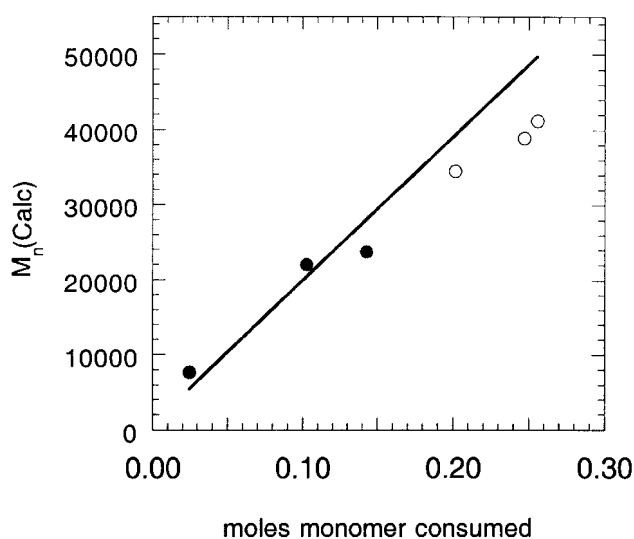


Figure 3. Calculated (—) and found molecular weights (g mol⁻¹) as a function of moles of monomer consumed during synthesis of polystyrene (●), then poly(methyl methacrylate)-*block*-polystyrene (○) by feed emulsion polymerization (refer to Table 6 and Experimental for conditions).

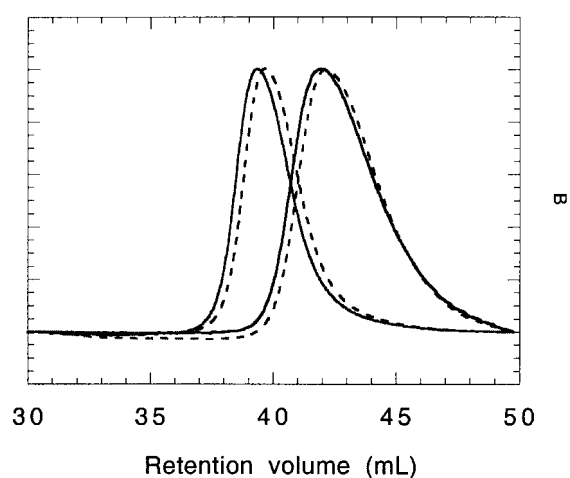


Figure 4. GPC traces of polystyrene (\bar{M}_n 7700, \bar{M}_w/\bar{M}_n 1.37) and poly(methyl methacrylate)-*block*-polystyrene (\bar{M}_n 41250, \bar{M}_w/\bar{M}_n 1.57) obtained by emulsion polymerization in the presence of benzyl dithioacetate (**2h**) using (a) RI detection (dashed line) and (b) UV (270 nm) detection (solid line); refer to Table 6. Offset in chromatograms is due to interdetector delay.

Time (min)	Monomer added (ml)		\bar{M}_n^b (g mol ⁻¹)	\bar{M}_w/\bar{M}_n	Conversion ^c (%)
	MMA	Styrene			
30	8	0	9400	1.22	43
60	16	0	25000	1.54	85
90	16	6	36000	1.68	>99
120	16	12	49400	1.86	>99
150	16	18	52100	2.07	>99
210	16	24	72500	2.24	>99
360	16	24	72100	2.21	>99

Table 7. Molecular weight and conversion obtained during synthesis of poly(methyl methacrylate)-*block*-polystyrene by emulsion polymerization in the presence of cumyl dithiobenzoate (**2a**) at 80 °C^a

^a For experimental conditions and reagent concentrations see Experimental.

^b Molecular weight in polystyrene equivalents.

^c Conversion of total monomers added.

as the RAFT agent⁴ or in solution experiments with cumyl dithiobenzoate (**2a**). To more firmly establish the block structure, the copolymers were again analysed by GPC with diode array detection. In this case, observation at 330 nm allowed detection of the end-group without interference from the polymer backbone and showed that block copolymer retains living chain-ends (see Fig. 6). The absorption maxima for the dithiobenzoate chromophore was also observed to shift consistently with it becoming attached to a polystyrene versus a poly(methyl methacrylate) chain-end on introduction of styrene monomer.

The emulsion polymerizations were carried out so as not to have a discrete monomer droplet phase other than during the initial stages of the polymerization. This necessitated the use of a seeded emulsion polymerization or a feed process as described above. Attempts at batch emulsion polymerization yielded less satisfactory results. Batch miniemulsion polymerizations (also characterized by the absence of a discrete monomer droplet phase) were possible and yielded narrow polydispersity polymers. Miniemulsion poly-

merizations of styrene and methyl methacrylate have been successfully carried out using reaction conditions based on those described by El-Aasser and co-workers.²¹ In the case of the styrene polymerization, significant retardation due to slow utilization of the RAFT agent phenylethyl dithiobenzoate (**2b**) was observed (see Table 8). The behaviour is analogous to that observed in solution polymerization (see above).

CONCLUSIONS

RAFT polymerization is arguably the most versatile and effective means of living free radical polymerization currently available. The versatility of the method is demonstrated by its compatibility with a very wide range of monomers and reaction conditions. This paper has highlighted some of the advantages and limitations and has shown that, with understanding of the mechanism and the factors that control the activity of RAFT agents, most limitations can be overcome.

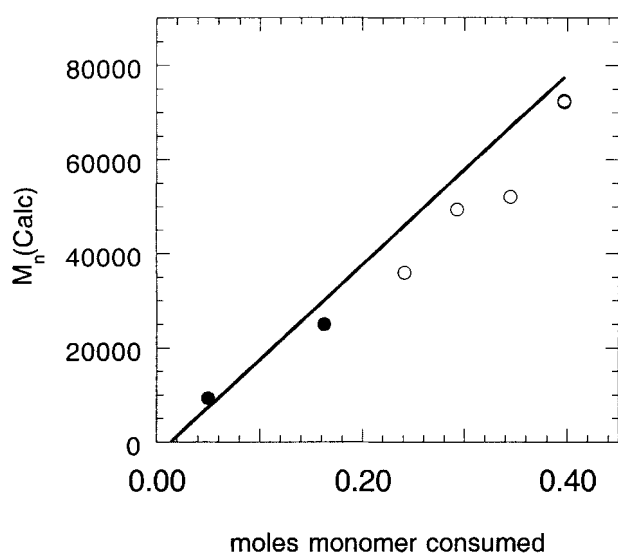


Figure 5. Calculated (—) and found molecular weights (g mol⁻¹) as a function of moles of monomer consumed during synthesis of poly(methyl methacrylate) (●) initially and then poly(methyl methacrylate)-*block*-polystyrene (○) by feed emulsion polymerization (refer to Table 7 and Experimental for conditions).

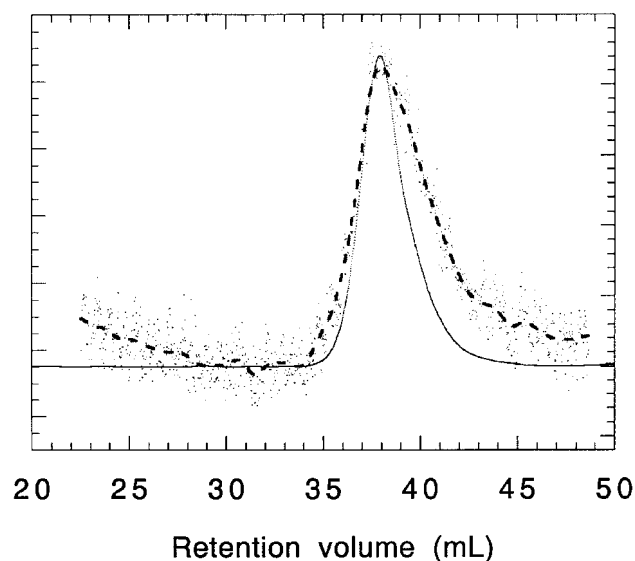


Figure 6. GPC traces of poly(methyl methacrylate)-*block*-polystyrene (\bar{M}_n 72500 g mol⁻¹, \bar{M}_w/\bar{M}_n 2.24) prepared by emulsion polymerization in the presence of cumyl dithiobenzoate (**2a**) (refer to Table 7) using RI detection (—) and UV (310 nm) detection (---). (The dashed line is a line of best fit through the data.)

Table 8. Molecular weight and conversion obtained during synthesis of polystyrene by miniemulsion polymerization in the presence of 1-phenylethyl dithiobenzoate (**2b**)^a

Time (min)	Control (no RAFT agent)			With 2b		
	\bar{M}_n (g mol ⁻¹)	\bar{M}_w/\bar{M}_n	Conversion (%)	\bar{M}_n (g mol ⁻¹)	\bar{M}_w/\bar{M}_n	Conversion (%)
30	–	–	–	3700	1.79	9
60	692200	1.86	82	2900	1.77	11
120	654100	2.08	>95	3150	1.39	16
240	442380	2.71	100	5980	1.18	25

^a Initiator: potassium persulfate, surfactant: sodium dodecyl sulfate/cetyl alcohol. For additional details see Experimental.

EXPERIMENTAL

General

Monomers were purified by filtration through alumina (to remove inhibitors), distilled and flash distilled immediately before use. Gel permeation chromatography was performed on a Waters Associates liquid chromatograph equipped with a differential refractometer and a set of Waters Ultrastaygel columns (10⁶, 10⁵, 10⁴, 10³, 500 and 100Å). Tetrahydrofuran (1.0 ml min⁻¹) was used as eluent. Conversions were determined gravimetrically. NMR spectra were obtained with a Bruker AC200 spectrometer on samples dissolved in deuteriochloroform. Chemical shifts are reported in ppm from TMS. High resolution chemical ionization mass spectra were obtained with a Jeol JMS DX303 mass spectrometer.

Synthesis of thiocarbonylthio compounds

Syntheses of cumyl and 2-cyanoprop-2-yl dithiobenzoate (**2a** and **2d**) are described below. The syntheses and characterization of other thiocarbonylthio compounds are given elsewhere.^{7,9,22}

2-Phenylprop-2-yl Dithiobenzoate (**2a**)

A mixture of dithiobenzoic acid²³ (10.59 g), α -methylstyrene (10 g) and carbon tetrachloride (40 ml) was heated at 70 °C for 4 h. The solvent and excess monomer were removed on a rotary evaporator and the residue purified by column chromatography on alumina (activity III) with *n*-hexane as eluent to give 2-phenylprop-2-yl dithiobenzoate (**2a**) (6.1 g, 32.6% yield) as a dark purple oil. ¹H NMR δ : 2.03 (s, 6H); 7.20–7.60 (m, 8H) and 7.86 (m, 2H). High resolution CI mass spectrum: found 273.0745 (M+1); C₁₆H₁₇S₂ requires 273.0772. Note that dithiobenzoic acid is unstable and should be used immediately or stored at low temperature.

2-Cyanoprop-2-yl Dithiobenzoate (**2d**)

A solution of phenyl magnesium bromide (from bromobenzene (3.1 g) and magnesium turnings (0.5 g) in dry tetrahydrofuran (20 ml) was warmed to 40 °C and carbon disulfide (30.4 g) was added over 15 min at such a rate that the reaction temperature was maintained at 40 °C. 2-Bromo-2-cyanopropane²⁴ (3 ml) was added to the resultant dark brown mixture over 15 min, after which the reaction temperature was raised to 50 °C and maintained at that temperature for 24 h. Ice water (30 ml) was added and the mixture

extracted with diethyl ether (total 75 ml). The combined ethereal extracts were washed with water, brine and dried over anhydrous magnesium sulfate. Purification by column chromatography (Kieselgel-60, 70–230 mesh) with *n*-hexane/diethyl ether (9:1) as eluent gave 2-cyanoprop-2-yl dithiobenzoate (**2d**) as a dark red oil (1.9 g, 43% yield). ¹H NMR δ : 1.95 (s, 6H, 2xCH₃), 7.38 (dd, 2H, *meta*-ArH), 7.57 (dd, 1H, *para*-ArH) and 7.92 (d, 2H, *ortho*-ArH). ¹³C NMR (CDCl₃) δ : 26.5 (CH₃), 41.7 (C(CN)), 120.0 (CN), 126.6, 128.5, 132.9, 144.5 (ArC) and 227 (C=S). High resolution CI mass spectrum: found 222.0387 (M+1); C₁₁H₁₁S₂N requires 222.0333.

Thermal styrene polymerizations

Aliquots (1–2 ml) of a stock solution of the thiocarbonylthio compound in styrene were transferred to ampoules. The ampoules were degassed by three freeze–evacuate–thaw cycles, and flame sealed. The ampoules were heated at 110 °C for the indicated times. Unconverted styrene was removed by evaporation and the residue analysed directly by GPC. Results are shown in Figs 1 and 2.

Retardation in solution polymerization

Aliquots (about 5 ml) of stock solution comprising initiator, solvent and monomer (15 g) were added to ampoules containing the appropriate amount of RAFT agent. The solutions were degassed through four freeze–thaw–evacuate cycles on a rotary/diffusion line, sealed under vacuum and then placed in a thermostatted bath at the appropriate temperature for the indicated times. Results for styrene and *n*-butyl acrylate polymerizations are shown in Tables 3 and 4, respectively.

Emulsion polymerization

Polystyrene

The following procedure illustrates the standard conditions for emulsion polymerization of styrene.

A five-necked reaction vessel equipped with a condenser, thermocouple and mechanical stirrer was charged with water (75 g) and sodium dodecyl sulfate (3 g of 10% aqueous solution). The solution was heated at 80 °C for 40 min while purging with nitrogen. 4,4'-Azobis(4-cyanopentanoic acid) (211 mg) and *O*-ethyl *S*-benzyl dithiocarbonate (**2l**) (198 mg) in styrene (4.7 g) were then added. Further styrene (39.2 g, 0.2 ml min⁻¹) and initiator (211 mg in 24 g of

1% (w/w) aqueous sodium dodecyl sulfate, 0.089 ml min⁻¹) were added by syringe pumps. After completion of the feeds, the reaction was held at 80°C for 90 min. The polymerization was sampled periodically to establish conversion and for GPC analysis.

Results for emulsion polymerizations with various thiocarbonylthio compounds are shown in Table 5.

Poly(methyl methacrylate)-block-polystyrene

(a) *Polystyrene block prepared first with benzyl dithioacetate (2h) as RAFT agent.* A five-necked reaction vessel equipped with a condenser, thermocouple and mechanical stirrer was charged with water (50 g) and sodium dodecyl sulfate (3.1 g of 10% aqueous solution). The solution was heated at 80°C for 40 min while purging with nitrogen. 4,4'-Azobis(4-cyanopentanoic acid) (88 mg) and benzyl dithioacetate (2h) (104 mg) in styrene (2.3 g) were then added. Further styrene (11.3 g, 0.2 ml min⁻¹) and initiator (531 mg in water 100 g, 0.089 ml min⁻¹) was added by syringe pump. The reaction temperature was then increased to 90°C and feeds of methyl methacrylate (14 g, 0.316 ml min⁻¹) and initiator (265 mg in water 100 g, 0.312 ml min⁻¹) were commenced. On completion of the feeds, the reaction was held at 90°C for a further 60 min. The polymerization was sampled periodically to establish conversion and for GPC analysis. Results are shown in Table 6.

(b) *Poly(methyl methacrylate) block prepared first with cumyl dithiobenzoate (2a) as RAFT agent.* A five-necked reaction vessel equipped with a condenser, thermocouple and mechanical stirrer was charged with water (37.5 g) and sodium dodecyl sulfate (3 g of 10% aqueous solution). The solution was heated at 80°C for 40 min while purging with nitrogen. 4,4'-Azobis(4-cyanopentanoic acid) (71 mg) and cumyl dithiobenzoate (2a) (18 mg) in methyl methacrylate (1.6 g) were then added. Further methyl methacrylate (2.5 g) and cumyl dithiobenzoate (108 mg) were added over 10 min by syringe pump. A feed of methyl methacrylate (10.9 g, 0.188 ml min⁻¹) was then commenced. On completion of this addition a feed of styrene (21.7 g, 0.2 ml min⁻¹) was commenced. Further initiator (31.5 mg) was added to the reaction mixture at 90 min intervals during the additions. On completion of the feed, the reaction was held at 80°C for a further 120 min. Results are shown in Table 7.

Miniemulsion polymerization of styrene

A mixture of water (75 g) sodium dodecyl sulfate (215 mg), cetyl alcohol (543 mg) and potassium persulfate (55 mg) was homogenized for 10 min. Using an Ultra Turrax Model T25 homogenizer with a H40-110 drive unit and an S25N-18G dispersing tool at 3000 rev min⁻¹. A solution of 1-phenylethyl dithiobenzoate (2b) (105 mg) in styrene (18.8 g) was then added and the mixture homogenized for a further 5 min. The mixture was then placed in a five-necked

reaction vessel equipped with a condenser, thermocouple and mechanical stirrer, and heated at 70°C. After 40 min the initiator, potassium persulfate (55 mg), was added. The polymerization was sampled at hourly intervals for GPC characterization.

A control experiment was carried out under similar conditions but without the RAFT agent. The results of both experiments are summarized in Table 8.

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REFERENCES

- 1 Matyjaszewski K, ACS Symp Series 685, American Chemical Society, Washington DC, 2 (1998).
- 2 Moad G and Solomon DH, *The Chemistry of Free Radical Polymerization*, Pergamon, Oxford, pp 315–351 (1995).
- 3 Krstina J, Moad G, Rizzardo E, Winzor CL, Berge CT and Fryd M, *Macromolecules* **28**:5381 (1995).
- 4 Krstina J, Moad CL, Moad G, Rizzardo E, Berge CT and Fryd M, *Macromol Symp* **111**:13 (1996).
- 5 Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, Mayadunne RTA, Meijs GF, Moad CL, Moad G, Rizzardo E and Thang SH, *Macromolecules* **31**:5559 (1998).
- 6 Chong BYK, Le TPT, Moad G, Rizzardo E and Thang SH, *Macromolecules* **32**:2071 (1999).
- 7 Le TP, Moad G, Rizzardo E and Thang SH, PCT Int Appl WO 98/01478; *Chem Abstr* **128**:115390 (1998).
- 8 Rizzardo E, Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, Mayadunne RTA, Meijs GF, Moad CL, Moad G and Thang SH, *Macromol Symp* **143**:291 (1999).
- 9 Chiefari J, Mayadunne RTA, Moad G, Rizzardo E and Thang SH, PCT Int. Appl. WO 99/31144; *Chem Abstr* **131**:45250 (1999).
- 10 Mayadunne RTA, Rizzardo E, Chiefari J, Moad G and Thang SH, *Macromolecules* **32**:6977 (1999).
- 11 Moad G, Moad CL, Rizzardo E and Thang SH, *Macromolecules* **29**:7717 (1996).
- 12 Moad G, Ercole F, Johnson CH, Krstina J, Moad CL, Rizzardo E, Spurling TH, Thang SH and Anderson AG, ACS Symp Series 685, Ed by Matyjaszewski, K, American Chemical Society, Washington DC, 332 (1998).
- 13 Quirk RP and Lee B, *Polym Int* **27**:359 (1992).
- 14 Matyjaszewski K and Mueller AHE, *Polym Prepr* **38**(1):6 (1997).
- 15 Hawthorne DG, Moad G, Rizzardo E and Thang SH, *Macromolecules*, **32**:5457 (1999).
- 16 Goto A, Sato K, Fukuda T, Moad G, Rizzardo E and Thang SH, *Polym Prepr* **40**(2):397 (1999).
- 17 Chong YK, Krstina J, Le TPT, Moad G, Rizzardo E and Thang SH, *Macromolecules* to be submitted (1999).
- 18 Chiefari J, Mayadunne RTA, Moad CL, Moad G, Postma A, Rizzardo E and Thang SH, *Macromolecules* to be submitted (1999).
- 19 Müller AHE, Zhuang R, Yan D and Litvenko G, *Macromolecules* **28**:4326 (1995).
- 20 Müller AHE and Litvenko G, *Macromolecules* **30**:1253 (1997).
- 21 Miller CM, Sudol ED, Silebi CA and E1-Aasser MS, *J Polym Sci Part A Polym Chem* **33**:1391 (1995).
- 22 Thang SH, Chong YK, Mayadunne RTA, Moad G and Rizzardo E, *Tetrahedron Lett* **40**:2435 (1999).
- 23 Becke F and Hagen H, Ger 1 274 121, (*Chem Abstr* **70**:3573v) (1968).
- 24 Chrzaszczewska A and Popiel J, *Roczniki Chem* **7**:74 (1927).