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## Dithiocarbamate RAFT agents with broad applicability – the 3,5-Dimethyl-1*H*-pyrazole-1-carbodithioates

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3,5-Dimethyl-1*H*-pyrazole-1-carbodithioates are shown to be extremely versatile dithiocarbamate RAFT agents with wide-spread applicability. The cyanomethyl and benzyl dithiocarbamates offer very low dispersities ( $\bar{D} < 1.1$ ) for polymers based on more activated monomers [MAMs: methyl acrylate (MA), *N,N*-dimethylacrylamide (DMA) and styrene (St)] and  $\bar{D} < 1.3$  in polymerization of vinyl acetate (VAc), a less activated monomer (LAM). The tertiary, 2-cyano-2-butyl dithiocarbamate, provides molar mass control and  $\bar{D} < 1.5$  in methyl methacrylate (MMA) polymerization. Lower dispersities can be obtained for MMA copolymers. End group fidelity was proved with the synthesis of block copolymers, poly(DMA)-*block*-poly(MA). With the ability to control polymerization of both MAMs and LAMs, the RAFT agents were also shown to be suitable for the synthesis of a poly(MAM)-*block*-poly(LAM), specifically poly(DMA)-*block*-poly(VAc). The RAFT agents are an appropriate replacement for trithiocarbonate RAFT agents in most circumstances and have the distinct advantage that the RAFT agents have low odour and the derived polymers do not develop odour on storage (i.e., no low molar mass thiols are generated).

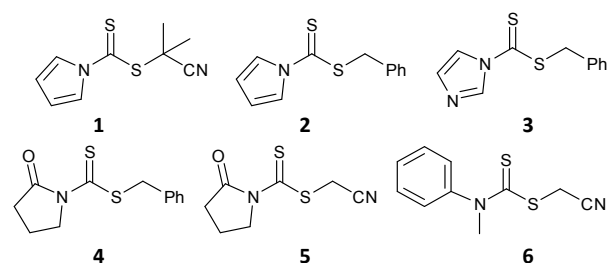
### Introduction

RAFT (Reversible Addition Fragmentation chain Transfer) polymerization is a Reversible Deactivation Radical Polymerization (RDRP);<sup>1</sup> a process which, with appropriate attention to reagents and reaction conditions, can possess most of the essential attributes of living polymerization. RAFT provides reversible deactivation by degenerate chain transfer. The chain transfer step is termed degenerate because the process involves only an exchange of functionality. The only distinction between the similar species on the two sides of the deactivation-activation equilibrium is their degree of polymerization. RAFT polymerization was first disclosed in 1995 with macromonomer RAFT agents,<sup>2-4</sup> and in 1998, with the more well-known, thiocarbonylthio RAFT agents.<sup>4</sup>

The impact of thiocarbonylthio RAFT polymerization can be attributed to that fact that the technique is applicable to a vast range of monomers under a wide range of reaction conditions.<sup>5-9</sup> The polymerization of most monomers amenable to radical polymerization can be controlled with appropriate selection of the RAFT agent. Specifically, RAFT was the first RDRP technique to offer control over the polymerization of less activated monomers (LAMs).<sup>10</sup> The original CSIRO patent<sup>11</sup> reported control over vinyl benzoate polymerization with 2-cyanoprop-2-yl dithiobenzoate [150 °C

in bulk to provide poly(vinyl benzoate)  $M_n$  3490,  $\bar{D}$  1.29, 25% conversion after 48 h (Example 62 of patent)].<sup>11</sup> However, it was soon recognized that dithiobenzoates, while they remain preferred for some applications, have significant limitations with respect to scope and utility.<sup>12</sup>

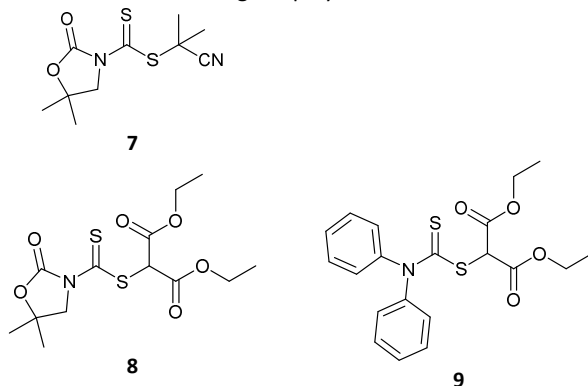
Dithiocarbamates were the one of the first classes of RAFT agent shown to have wide applicability with respect to monomer type. Dithiocarbamate RAFT agents were the subject of patent applications by CSIRO-DuPont (US6642318,<sup>13</sup> priority 11 Dec 1998) and Rhodia (US6812291,<sup>14</sup> priority 23 Dec 1998) the original versions of which were filed almost simultaneously at the end of 1998. Publications by the groups at CSIRO<sup>15,16</sup> and Rhodia<sup>17</sup> on the material covered by these patents followed during 1999-2000.



The CSIRO work showed that, with appropriate choice of substituents on nitrogen, control could be obtained over both more activated monomers (MAMs) and LAMs.<sup>16</sup> The RAFT agents in which the dithiocarbamate nitrogen lone pair was part of an aromatic ring system, e.g., pyrrole (1, 2) or imidazole (3), provided control of MAMs, styrene (St)<sup>15,18</sup> and ethyl acrylate (EA),<sup>15</sup> whereas RAFT agent 6 gave good control (low

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$\bar{D}$ ) in the polymerization of vinyl acetate (VAc, a LAM).<sup>16</sup> The 2-cyanopropan-2-yl 1*H*-pyrrole-1-carbodithioate (**1**) also provided good control over methyl methacrylate (MMA) polymerization.<sup>19</sup> It was also found that dithiocarbamates with a carbonyl alpha to the dithiocarbamate nitrogen (e.g., **4**, **5**) were effective in mediating the polymerization of MAMs.<sup>13</sup>



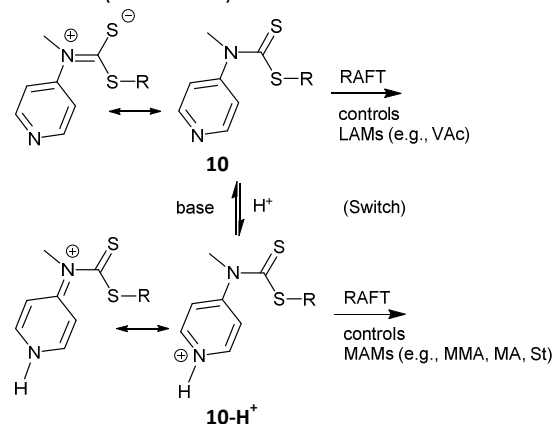
The Rhodia study<sup>17</sup> showed RAFT that agents containing the 5,5-dimethyloxazolidin-2-one Z group (**7**, **8**) provided control (molar mass consistent with prediction,  $\bar{D} < 1.2$ ) over the polymerization of St, EA and VAc. The RAFT agent **7** also gave some control over MMA polymerization in that molar mass control was observed,<sup>17</sup> although  $\bar{D}$  was  $> 1.7$ . Also reported in the paper was the RAFT agent **9**, which provided modest control ( $\bar{D} \sim 1.4$ , molar mass consistent with prediction) over the polymerization of both EA and VAc.

Shipp and coworkers<sup>20,21</sup> further explored the use of diphenyl dithiocarbamate **9** and several other dithiocarbamates in the context of controlling polymerization of VAc confirming the findings of the Rhodia study. The RAFT agent **9** was also used successfully to synthesize poly(St)-*block*-poly(VAc).<sup>21</sup>

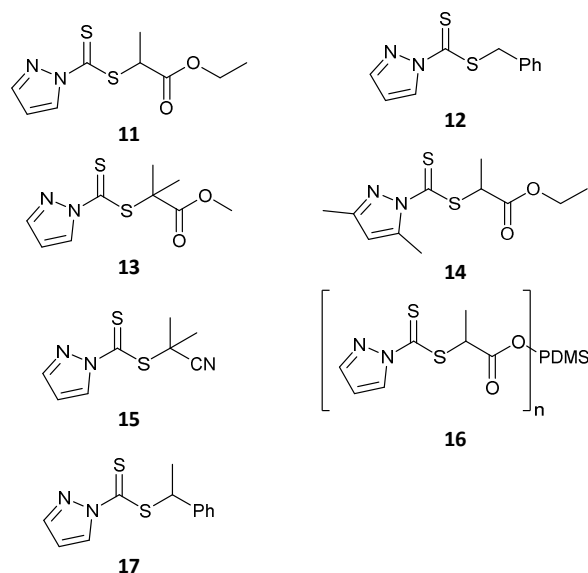
Xanthates can be similarly tuned to have wide utility with selection of the *O*-alkyl substituent.<sup>22</sup> The so-called F-RAFT was initially promoted as a universal RAFT agent with ability to control the polymerization of both LAMs and MAMs.<sup>23,24</sup> However, difficulties in RAFT agent synthesis have prevented experimental demonstration of promised versatility of this reagent.

The above-mentioned studies demonstrate that while dithiocarbamate RAFT agents can be designed to provide good control (i.e. very low  $\bar{D}$ , high end group fidelity, predictable molar mass) over the polymerization of LAMs or MAMs, or modest control over the polymerization of both classes of monomer. However, it was not possible to achieve good control (in particular very low  $\bar{D}$ ) over both classes of monomer with a single RAFT agent. In response to this challenge, switchable RAFT agents were introduced<sup>25-27</sup> mainly to provide for the synthesis of poly(MAM)-*block*-poly(LAM) with low dispersity. The neutral *N*-methyl-*N*-(4-pyridinyl)dithiocarbamates (**10**, Scheme 1) have properties similar to those of 1-3 and provide control over polymerization of LAMs. The protonated *N*-methyl-*N*-(4-pyridinium)dithiocarbamates (**10-H<sup>+</sup>**), which are simply formed by addition of an equivalent of a strong acid, have properties

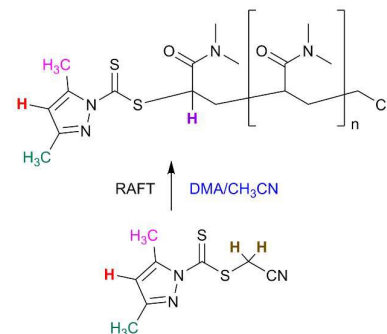
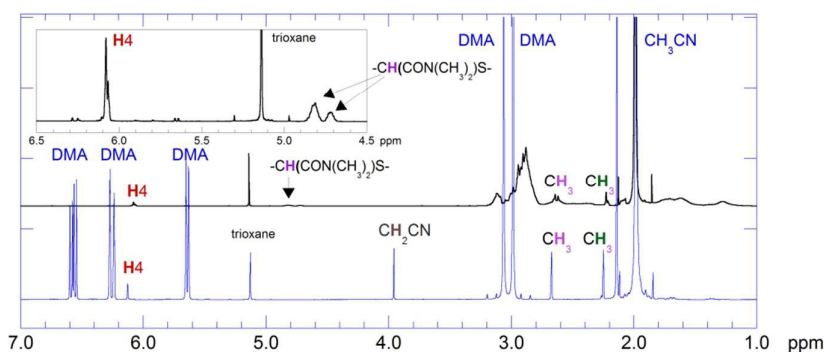
analogous to **6** and are effective in controlling the polymerization of MAMs.<sup>25-30</sup> The *N*-aryl-*N*-(4-pyridinyl)dithiocarbamates<sup>31,32</sup> are more active with MAMs in protonated (switched) form and more active with LAMs in non-protonated (unswitched) form.



**Scheme 1.** Switchable *N*-methyl-*N*-(4-pyridinyl)dithiocarbamate RAFT agents (**10**). R is a good homolytic leaving group capable of efficiently initiating polymerization of the chosen monomer(s).



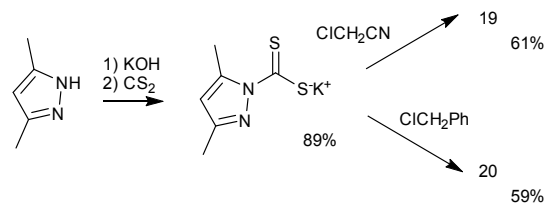
The use of 1*H*-pyrazole-1-carbodithioates as RAFT agents was first reported by Charmot and coworkers at Symyx.<sup>33-39</sup> Patents issued to Symyx<sup>33-35</sup> describe the synthesis of RAFT agents **11** and **12** and their use in controlling polymerization of butyl acrylate and St. Subsequent work<sup>37,38</sup> described end group removal,<sup>36</sup> the use of RAFT agents **11**, **13**, **14** and **15** in synthesis of acrylate/methacrylate copolymers for use in photoresists, and the preparation of poly(dimethyl siloxane) blocks (derived with use of **16**) for use in laundry applications.<sup>39</sup> The only report on the use of 1*H*-pyrazole-1-carbodithioates as RAFT agents in the open literature is of Babu and Dhamodharan's experiments<sup>40</sup> with **11** and **17** in polymerization of St and 2-vinylpyridine.



Scheme 2. RAFT polymerization of *N,N*-dimethylacrylamide (DMA).

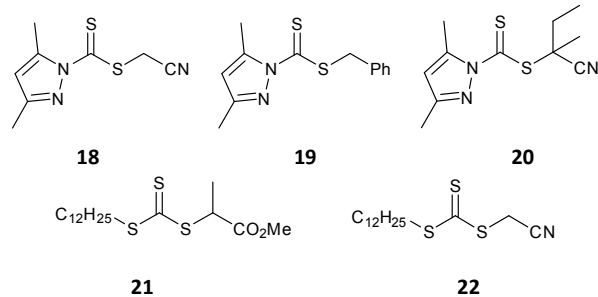
**Figure 1.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) of polymerization mixture at time = 0 (lower) and time = 1 h (upper) for polymerization of *N,N*-dimethylacrylamide (DMA) in the presence of RAFT agent **18** in acetonitrile as solvent at  $100^\circ\text{C}$ . The product is poly(DMA)  $M_n \sim 2600$  (3<sup>rd</sup> row Table 1). The inset shows an expansion of the region 6.5–4.5 ppm of the time = 1 h spectrum. The signals labelled H4 and CH<sub>3</sub> are attributed to the 3,5-dimethyl-1*H*-pyrazole group, that labelled  $-\text{CH}(\text{CON}(\text{CH}_3)_2)\text{S}-$  is the chain end methine (refer Scheme 2). Trioxane is present as an internal standard.

In this paper, we further explore the utility of 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates as RAFT agents. In particular, their use to control the polymerization of both MAMs (MMA, methyl acrylate (MA), *N,N*-dimethylacrylamide (DMA), and St) and VAC (a LAM) to give low dispersity polymers and a viable route to poly(MAM)-*block*-poly(LAM).



Scheme 3. Synthesis of 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates.

## Results and discussion



The primary (e.g., **18**, **19**) and secondary 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates are readily prepared by alkylation of the carbodithioate salt (Scheme 3).<sup>34,41</sup> We used the chloro-compounds as alkylating agents, which may provide a lower yield than the corresponding bromo-compounds, but are more cost effective. The benzyl derivative has been previously prepared by condensation of 2,4-pentanedione with benzyl hydrazinecarbodithioate.<sup>42–44</sup> Tertiary dithiocarbamates (e.g., **20**) can be prepared by radical-induced decomposition of the bis(thioacyl) disulfide, where radicals are conveniently generated from the appropriate dialkyldiazene.<sup>45–47</sup>

The use of these RAFT agents was explored in polymerization of DMA, MMA, MA, St and VAC. All polymerizations were carried out in a microwave reactor at  $100^\circ\text{C}$  (unless indicated) with 1,1'-azobis(-1-cyanocyclohexane) (ACHN) as initiator. We have previously demonstrated no “microwave effect” in RAFT polymerization with other RAFT agents<sup>48</sup> and therefore would anticipate similar results for experiments conducted in batch with conventional heating or in continuous flow, subject to the limitations of those methods. We also expect no significant “pressure effect” due to the slightly raised pressures caused by the polymerizations being conducted in sealed vessels above the boiling point of the monomer/solvent. Results are summarized in Table 1 (homopolymerizations), Table 2 (copolymerizations) and Table 3 (block copolymers). The polymerization conditions chosen for our screening experiments were initially selected to provide very rapid polymerization of DMA and MA as required for flow chemistry experiments (relatively high initiator concentrations were used).<sup>48</sup>

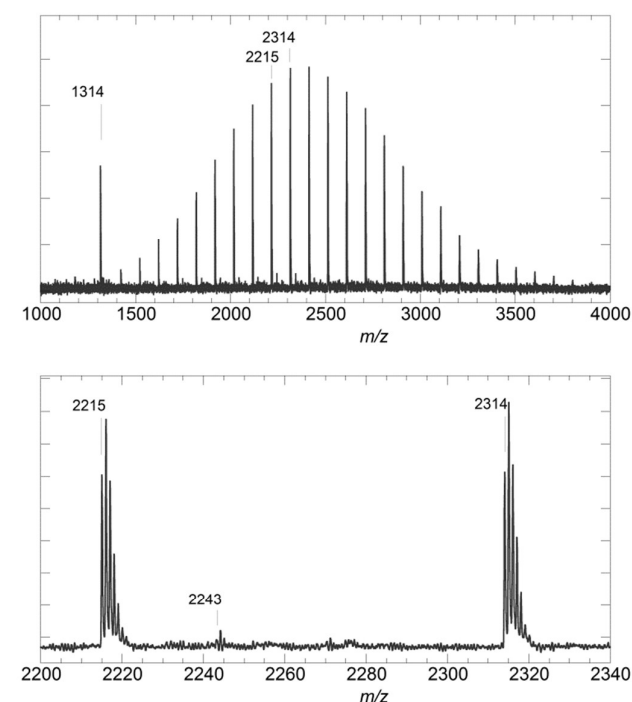
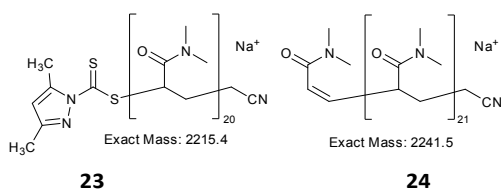
The fraction of living chains or end group fidelity ( $L$ ) obtained in the various experiments was estimated using eqn. 1.

$$L = \frac{[\text{RAFT}]_0}{[\text{RAFT}]_0 + df[I_2]_0(1 - e^{-k_d t})} \quad (1)$$

where  $[\text{RAFT}]_0$  and  $[I_2]_0$  are the initial concentrations the RAFT and initiator, respectively,  $d$  is the number of chains formed in termination,  $f$  is the overall initiator efficiency,  $k_d$  is the rate

coefficient for initiator decomposition, and  $t$  is the reaction time. Values are provided in the Tables. The value of  $f$  for ACHN at 100 °C is not known. The low conversion initiator efficiency has been reported in the range 0.6–0.65 at 80 °C.<sup>49,50</sup> It might be expected to be higher at higher temperatures and to reduce for very high monomer conversions. For the purposes of estimating  $L$  and for the evaluation of  $M_n(\text{calc})$  we have assumed a value of  $f$  of 0.7. The values of  $k_d$  ( $9.59 \times 10^{-5} \text{ s}^{-1}$  at 100 °C and  $2.54 \times 10^{-5} \text{ s}^{-1}$  at 90 °C) are based on a soon to be published critical assessment of the literature data.<sup>51</sup>

Values of  $C_{tr}$  estimated on the basis of the measured monomer conversion, dispersity and molar mass values are also indicated in Table 1 (see Supporting Information).

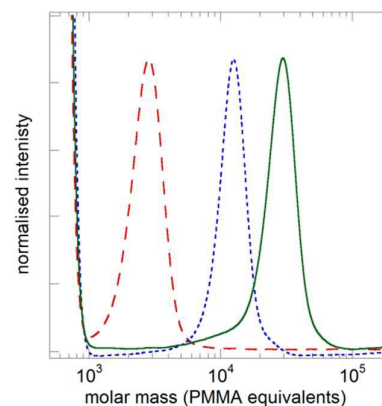


**Figure 2.** MALDI mass spectrum of poly(*N,N*-dimethylacrylamide)  $M_n \sim 2600$  formed with RAFT agent **18** (3<sup>rd</sup> row Table 1) obtained with Bruker Autoflex III smartbeam MALDI TOF-TOF operating in positive ion reflectron mode with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene]malononitrile (DCTB) matrix. The major peaks in the distribution correspond to  $M+23$  ( $M+\text{Na}$ ) for the target polymer ( $m/z = ((171.0+40)+(n \times 99.1)+23) = 2215$  for  $n=20$ , refer structure **23**). A second very minor population may correspond to the species formed by loss of the 1*H*-pyrazole-1-carbodithioate radical (e.g., **24**). The peak labelled 1314 is an artefact.

The  $^1\text{H}$  NMR spectra of the polymerization mixture used to prepare lower molar mass PDMA with **18**, before and after a polymerization time of 1 h, are shown in Figure 1. The final spectrum is consistent with the essentially quantitative

conversion of the RAFT agent to a poly(DMA) macro-RAFT agent. The calculated end group fidelity ( $L$ ) for this sample is 0.96. All signals associated with the chain-end, the 3,5-dimethyl-1*H*-pyrazole-1-carbodithioate group,  $2\text{xCH}_3$  and H4, and the  $\alpha$ -methine,  $-\text{CH}(\text{CON}(\text{CH}_3)_2)\text{S}-$ , appear as two peaks in a  $\sim 2:1$  ratio for the two chain-end diastereomers.

MALDI-TOF mass spectrometry analysis was performed on the same low molar mass poly(DMA). The mass spectrum shows a symmetrical distribution with one major population corresponding to the  $M+23$  (+sodium) adduct of the macro-RAFT agent. Within the population distribution, the peaks are separated by  $99.1 \text{ g mol}^{-1}$  corresponding to the molar mass of DMA (see Figure 2). These observations are consistent with the high end-group fidelity ( $L=0.96$ , refer Table 1) and demonstrate that the 3,5-dimethyl-1*H*-pyrazole-1-carbodithioate end groups of the poly(DMA) are retained largely intact under the polymerisation conditions used.



**Figure 3.** Molar mass distributions for poly(*N,N*-dimethylacrylamide) prepared with different concentrations of RAFT agent [**18**] = 0.006 (—), 0.01 (---) or 0.03 M (- - -), all with [ACHN] = 0.0006M). The large peak with apparent molar mass  $< 10^3$  poly(MMA) equivalents is a “salt peak” associated with the LiBr/DMAc SEC eluent.

The activities of the RAFT agents **18–20** in controlling polymerizations of DMA, MA and St are similar to those seen with the corresponding trithiocarbonates with dispersities ( $D$ )  $< 1.1$  being achieved (Table 1). For the highest molar mass targeted ( $M_n \sim 40000$ ) some tailing to low molar mass was observed (Figure 3). This may be indicative of the contribution of initiator-derived chains.

In marked contrast to similar trithiocarbonates, the RAFT agents **18–20** also provide a level of control over VAC polymerization with  $D < 1.3$  being obtained. Trithiocarbonates, such as **21** and **22**, completely inhibit polymerization of VAC and other LAMs under similar conditions.<sup>52</sup>

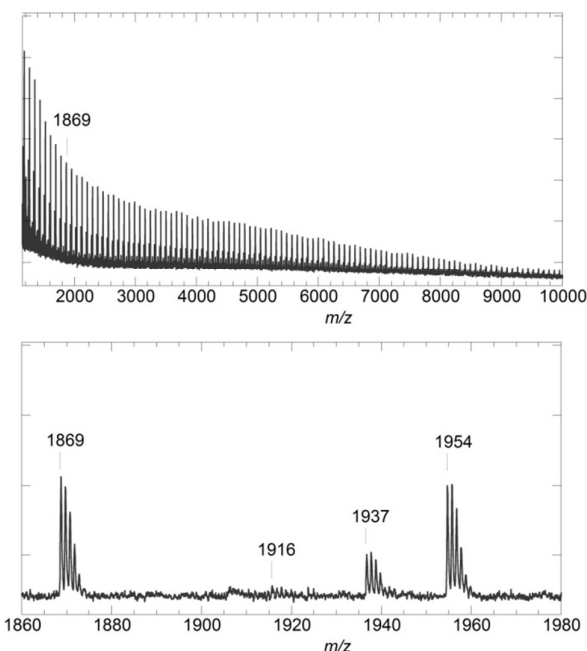
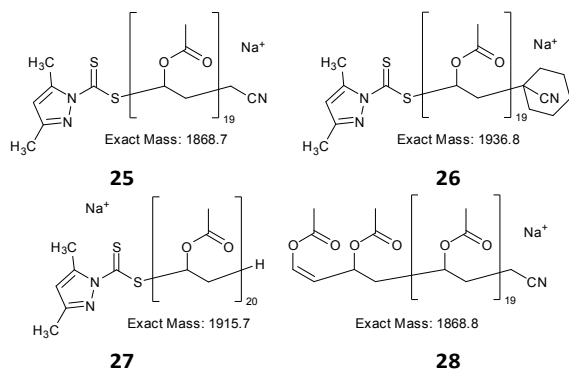


Figure 4. MALDI mass spectrum of poly(vinyl acetate)  $M_n \sim 7300$  formed with RAFT agent **18** (3<sup>rd</sup> entry for VAc, Table 1) obtained with Bruker Autoflex III smartbeam MALDI TOF-TOF operating in positive ion reflectron mode with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix. The major peaks in the distribution correspond to  $M+23$  ( $M+Na$ ) for the target polymer ( $m/z = ((171+40)+(n \times 86.0))+23 = 1869$  for  $n = 19$ , refer structure **25**) the initiator derived chains ( $m/z = ((171+108)+(n \times 99.1))+23 = 1937$  for  $n=19$ , refer structure **26**). See Text.

The major distribution in MALDI mass spectrum of poly(VAc) formed with RAFT agent **18** corresponds to  $(M+Na)$  for the target polymer,  $m/z = ((171+40)+(n \times 86.0))+23$ , refer structure **25**. Note, however, that the species formed by loss of 1*H*-pyrazole-1-carbodithioate group (refer structure **28**) have a very similar molar mass. A second distribution corresponds to the initiator-derived chains,  $m/z = ((171+108)+(n \times 86.0))+23$ , refer structure **26**. There is also some evidence for "hydrogen-atom" initiated chains,  $m/z = ((171+1)+(n \times 99.1))+23$ , refer structure **27**. However, we do not exclude the presence of chains formed by transfer to monomer<sup>53</sup> (expected at  $m/z = ((171-1)+(n \times 99.1))+23$ ).

The polymerization of VAc is substantially retarded with respect to a similar polymerization without RAFT or with the *N*-phenyl-*N*-methylthiocarbamate **6** (Table 1). Retardation in

RAFT polymerization of VAc reflects the stability of the intermediate formed by addition to the RAFT agent and the effect of this on side reactions involving that radical.<sup>10,54</sup> The dithiocarbamate **6** is well-suited to mediating the polymerization of LAMs but provides only very poor control over polymerization of MAMs, DMA and MA, with  $\bar{D} > 1.6$  being observed in those cases. The estimated  $C_{tr}$  for **6** in polymerization of DMA and MA are  $< 2$  (Table 1) vs  $\sim 15$ –30 for **18**–**20**. Dithiocarbamate **6** is essentially inert in batch MMA polymerization.

The benzyl dithiocarbamate **19** appeared equivalent to the cyanomethyl dithiocarbamate **18** in polymerization of MAMs, MA and DMA, but gave greater retardation when used to mediate VAc polymerization (a lower conversion after a longer reaction time – refer Table 1). This can be attributed to the benzyl radical adding only slowly to VAc and being a poor initiating radical in VAc polymerization.<sup>52</sup>

The tertiary dithiocarbamate (**20**) provided only limited control in MMA polymerization as indicated by relatively high dispersities ( $\bar{D} > 1.4$ ). This suggests a relatively low value of  $C_{tr}$  for **20** in MMA polymerization at 100 °C ( $C_{tr}$  estimated as ca. 3.7 Table 1). Low dispersities, e.g.,  $\bar{D} < 1.1$  with  $X_n = 150$  at 75% conversion, would require a  $C_{tr}$  of  $> 20$ .<sup>18</sup>

As would be expected, lower dispersities were achieved for copolymers of MMA with monosubstituted monomers, DMA or St (Table 2). In RAFT copolymerization, the dispersity is generally dictated by the monomer with the higher transfer constant. However, low dispersities will only be achieved whilst some of the comonomer remains. For MMA-DMA copolymerization the literature reactivity ratios ( $r_{MMA} = 2.36$ ,  $r_{DMA} = 0.34$ )<sup>55</sup> suggest that MMA should be consumed more rapidly than DMA. However, for an experiment with a MMA:DMA feed ratio of 93:7 after 4 h reaction time, the DMA was almost completely (99%) consumed whilst the conversion of MMA was only 68%. The dispersity achieved was 1.45. A lower dispersity (1.18) was achieved for a 1:1 MMA:DMA copolymer. However, the DMA was again ca. 99% consumed after 4 h during which time there was 90% conversion of the MMA. A dispersity of 1.15 was achieved for a 1:1 MMA:St copolymer. Studies aimed at establishing the time conversion profile for various monomers in copolymerization are planned.

Copolymers of VAc with DMA were also prepared. The dispersities obtained were low, however, significant retardation is still clearly evident (Table 2), Preferential consumption of the DMA is expected in these experiments (*vide infra*).

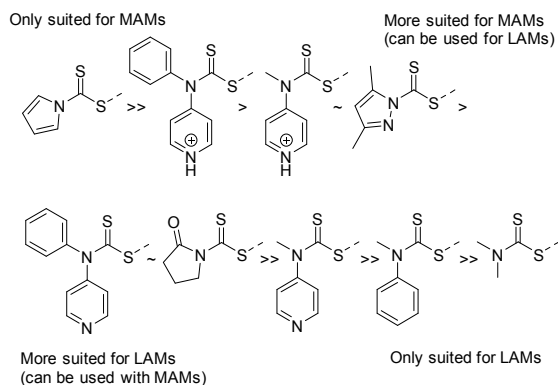


Figure 5. Relative activity of dithiocarbamate 'ZC(=S)S-' groups in RAFT polymerization. MAM – more activated monomer, LAM less activated monomer (see text).

The data from the present and previous studies<sup>15,18,25,31</sup> suggest an order of activity for dithiocarbamate RAFT agents shown in Figure 5. It appears the 3,5-dimethyl-1*H*-pyrazole-1-carbodithioates are less active as RAFT agents than the corresponding pyrrolocarbodithioates (e.g., 1) or the protonated (switched) form of **10-H<sup>+</sup>**. With appropriate choice of 'R', the latter RAFT agents provide low dispersities in MMA polymerization. The relative activity of dithiocarbamates can be understood in terms of the ability of the substituent to control the availability of the nitrogen lone pair and disfavor delocalization of the lone pair into the dithiocarbonyl double bond (refer Figure 6).

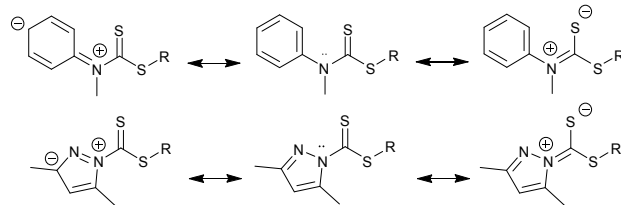


Figure 6. Some canonical forms of dithiocarbamates

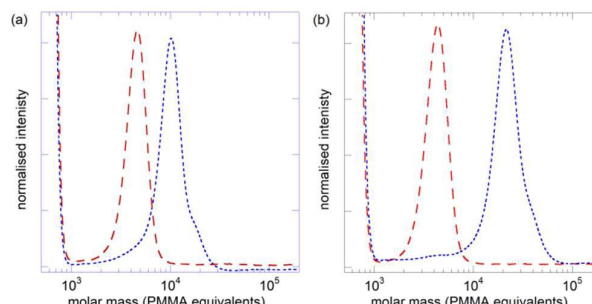


Figure 7. Molar mass distributions for poly(*N,N*-dimethylacrylamide) macro-RAFT agent prepared with RAFT agent **18** (---) and the derived poly(*N,N*-dimethylacrylamide)-*block*-poly(methyl acrylate) (- - -). Refer to (a) entry 1 and (b) entry 2 of Table 3. The large peak with apparent molar mass < 10<sup>3</sup> poly(MMA) equivalents is a "salt peak" associated with the LiBr/DMAc SEC eluent.

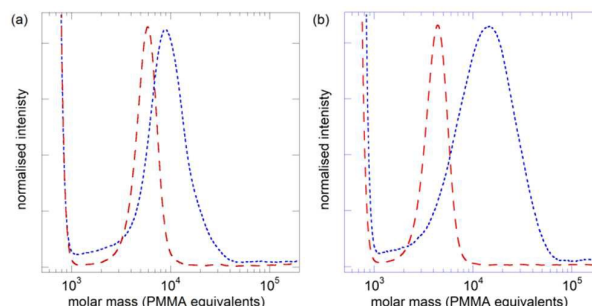


Figure 8. Molar mass distributions for poly(*N,N*-dimethylacrylamide) macro-RAFT agent prepared with (a) RAFT agent **20** or (b) **18** (---) and the derived poly(*N,N*-dimethylacrylamide)-*block*-poly(vinyl acetate) (- - -). Refer to (a) entry 6 and (b) entry 4 of Table 3. The large peak with apparent molar mass < 10<sup>3</sup> poly(MMA) equivalents is a "salt peak" associated with the LiBr/DMAc SEC eluent.

The RAFT agents allow the synthesis of poly(MAM)-*block*-poly(MAM), e.g., poly(DMA)-*block*-poly(MA). More importantly, they possess a balance of properties that allows the synthesis of poly(MAM)-*block*-poly(LAM), e.g. poly(DMA)-*block*-poly(VAc), without a need for switching (Table 3).

All block copolymers were prepared as "quasi-blocks".<sup>56-58</sup> In our "quasi-block" process, the macro-RAFT agent was not isolated. The process involved adding the monomer for the second block along with further initiator if required. The medium was then degassed and the polymerization continued for the time indicated. Our usage of the term "quasi-block" is distinct to that used in other contexts to describe systems which comprise a supramolecular polymer.<sup>59</sup>

Typical examples are shown in Figure 7, for poly(DMA)-*block*-poly(MA), and Figure 8, for poly(DMA)-*block*-poly(VAc). In the quasi-blocks, the second block will be a gradient copolymer (e.g., poly(DMA)-*block*-poly(VAc-*grad*-DMA)) and the monomer sequence will depend on the reactivity ratios. Reactivity ratios for DMA and VAc are not available. Those for *N*-acryloylpiperidine (NAPi) and VAc, which may be similar, are  $r_{\text{NAPi}} = 8.26$  and  $r_{\text{VAc}} = 0.0$ .<sup>60</sup> These values indicate that the DMA will be rapidly consumed during the early stages of copolymerization. Such reactivity ratios would also explain the finding, mentioned above, that addition of DMA as a comonomer has little influence on the rate of polymerization.

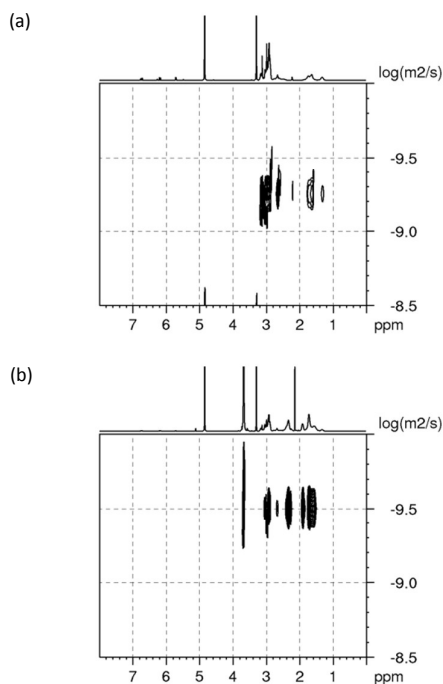


Figure 9.  $^1\text{H}$  DOSY spectra ( $\text{CD}_3\text{OD}$ , 500 MHz, 298 K) for (a) poly(*N,N*-dimethylacrylamide) macro-RAFT agent prepared with RAFT agent **18** and (b) the derived poly(*N,N*-dimethylacrylamide)-block-poly(methyl acrylate). The conditions used are reported in the Experimental. Sharp  $^1\text{H}$  NMR signals at  $\delta$  3.30 and 4.86 are attributable to the H impurity in the  $\text{CD}_3\text{OD}$  solvent. Those in spectrum (a) at  $\delta$  6.74, 6.18, 5.71 ( $\text{CH}_2=\text{CH}-$ ), 3.12 and 2.99 ( $2 \times \text{CH}_3$ ) are associated with the residual DMA.

A trace of the macro-RAFT agent is evident in the Molar mass distribution for the poly(DMA)-block-poly(MA) shown in Figure 7b. This is consistent with the estimated end group fidelity ( $L=0.97$ ). Some tailing to low molar mass may be attributed to the contribution of initiator-derived chains. A higher molar mass shoulder is seen in both Figure 7a and b. The large size of this shoulder, when considered in conjunction with the value of  $L$  (Table 3), which indicates that the maximum amount of termination product should be substantially less than 2 mole%, means that it should not be attributed to the product formed in termination by combination. It may be attributed to other processes known to cause bimodal distribution in RAFT polymerization of acrylates taken to higher conversions as discussed in earlier publications.<sup>61</sup> The purity of the poly(DMA)-block-poly(MA) was supported by DOSY NMR analysis, which also shows no sign of the precursor (<20%) and only one population of polymer species (Figure 9).

There is no indication of residual macro-RAFT agent in the Molar mass distributions for poly(DMA)-block-poly(VAc) shown in Figure 8. However, this would most likely be masked by the relatively high dispersity of the blocks. The pre-tailing evident in the traces can most likely be attributed to poly(VAc) homopolymer chains formed from initiator-derived radicals during block synthesis. The importance of this issue will be aggravated by retardation that is evident in VAc polymerization with the 1*H* pyrazole-1-carbodithioate RAFT agents. The dispersities reported in Table 3 for the poly(DMA)-block-poly(VAc) are underestimated because of the intrusion of the "salt peak" associated with the LiBr/DMAc SEC eluent. A  $^1\text{H}$  DOSY spectrum (Figure 10) for the block copolymer is consistent with there being only one major macromolecular species in the sample.

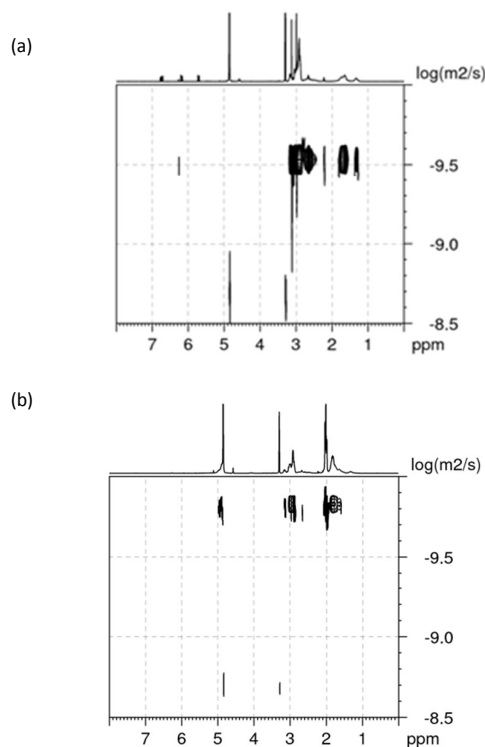


Figure 10.  $^1\text{H}$  DOSY spectra ( $\text{CD}_3\text{OD}$ , 500 MHz, 298 K) for (a) poly(vinyl acetate) macro-RAFT agent prepared with RAFT agent **18** and (b) the derived poly(*N,N*-dimethylacrylamide)-block-poly(vinyl acetate) (entry 4 of Table 3). The conditions used are reported in the Experimental. Sharp  $^1\text{H}$  NMR signals at  $\delta$  3.30 and 4.86 are attributable to the H impurity in the  $\text{CD}_3\text{OD}$  solvent. Those in spectrum (a) at  $\delta$  6.74, 6.18, 5.71, 3.12 and 2.99 are associated with the residual DMA. A signal at  $\delta$  6.27 is associated with the end group.



Polymer Chemistry

ARTICLE

**Table 1.** RAFT homopolymerizations in presence of 3,5-dimethyl-1H-pyrazole-1-carbodithioates **18-20**, dithiocarbamate **6** or trithiocarbonates **21** or **22**.<sup>a</sup>

monomer	[monomer] (M)	RAFT agent	[RAFT] (M)	[ACHN] <sup>b</sup> (M)	solvent <sup>b</sup>	time (h)	conv (%)	$M_n^c$	$M_n$ (calcd) <sup>d</sup>	$\bar{D}$	$L^e$	$C_{tr}^f$
DMA	3.0	<b>18</b>	0.03	0.006	CH <sub>3</sub> CN	1	99	12100	9641	1.07	0.96	17
DMA	3.0	<b>18</b>	0.03	0.003	CH <sub>3</sub> CN	1	99	11800	9830	1.06	0.98	20
DMA	3.0	<b>18</b>	0.15	0.03	CH <sub>3</sub> CN	1	99	2600	2098	1.07	0.96	(32)
DMA	3.0	<b>18</b>	0.03	0.0006	CH <sub>3</sub> CN	1	96	11500	9690	1.05	0.99 <sub>5</sub>	26
DMA	3.0	<b>18</b>	0.01	0.0006	CH <sub>3</sub> CN	1	86	24000	25479	1.11	0.99	(13)
DMA	3.0	<b>18</b>	0.006	0.0006	CH <sub>3</sub> CN	1	87	40800	42471	1.14	0.98	(9)
DMA	3.0	<b>19</b>	0.03	0.006	CH <sub>3</sub> CN	1	99	10400	9690	1.07	0.96	17
DMA	3.0	<b>20</b>	0.03	0.006	CH <sub>3</sub> CN	1	99	11000	9681	1.07	0.96	17
DMA	3.0	<b>20</b>	0.03	0.003	CH <sub>3</sub> CN	1	99	11200	9870	1.08	0.98	14
DMA	3.0	<b>6</b>	0.03	0.006	CH <sub>3</sub> CN	1	99	12800	9650	1.65	0.96	2
DMA	3.0	<b>21</b>	0.03	0.006	CH <sub>3</sub> CN	1	98	10700	9697	1.07	0.96	17
DMA	3.0	<b>22</b>	0.03	0.006	Acetone	1	99	12700	9746	1.09	0.96	12
MA	3.0	<b>18</b>	0.03	0.006	CH <sub>3</sub> CN	1	77	8600	6581	1.12	0.96	15
MA	3.0	<b>18</b>	0.03	0.003	CH <sub>3</sub> CN	1	71	6800	6203	1.10	0.98	21
MA	3.0	<b>18</b>	0.03	0.0006	CH <sub>3</sub> CN	1	47	5700	4242	1.15	0.99 <sub>5</sub>	24
MA	3.0	<b>19</b>	0.03	0.006	CH <sub>3</sub> CN	1	79	7100	6796	1.12	0.96	14
MA	3.0	<b>20</b>	0.03	0.006	CH <sub>3</sub> CN	1	83	7200	7118	1.08	0.96	21
MA	3.0	<b>6</b>	0.03	0.006	CH <sub>3</sub> CN	1	88	13400	7500	1.96	0.96	1
MA	3.0	<b>21</b>	0.03	0.006	CH <sub>3</sub> CN	1	81	6400	7064	1.06	0.96	32
St	3.5	<b>18</b>	0.0525	0.00525	Toluene	48	52	5200	3584	1.10	0.93	36
St	3.5	<b>20</b>	0.0525	0.00525	Toluene	48	63	5500	4337	1.07	0.93	43
MMA	6.55	<b>18</b>	0.0495	0.0018	CH <sub>3</sub> CN	6 (90°C)	53	441900	7184	2.71	-	-
MMA	6.55	<b>20</b>	0.0495	0.0018	CH <sub>3</sub> CN	6 (90°C)	74	17400 <sup>g</sup>	9987	1.44 <sup>g</sup>	0.98	4
VAc	3.0	<b>18</b>	0.048	0.012	EtOAc	12	62	5000	3059	1.29	0.85	8
VAc	3.0	<b>18</b>	0.03	0.0045	EtOAc	12	47	5900	3880	1.27	0.91	13
VAc	5.43	<b>18</b>	0.05	0.0084	EtOAc	12	64	7300	5576	1.51	0.90	4
VAc	5.43	<b>18</b>	0.0125	0.0084	EtOAc	12	87	24700	22453	1.56	0.68	(2)
VAc	3.0	<b>19</b>	0.048	0.012	EtOAc	24	49	3300	2506	1.07	0.85	70
VAc	3.0	<b>20</b>	0.048	0.012	EtOAc	48	57	4600	2864	1.17	0.85	17
VAc	3.0	<b>6</b>	0.048	0.012	EtOAc	2	85	6200	4429	1.18	0.92	8

<sup>a</sup> All experiments were conducted with microwave heating at 100 °C unless indicated. Control experiments with dithiocarbamate **6** and trithiocarbonates **21** or **22** are greyed. All concentrations are based on the mass or volume of material used at 22 °C and do not take into account volume of mixing effects. <sup>b</sup> ACHN = 1,1'-azobis(-1-cyanocyclohexane), EtOAc – ethyl acetate. <sup>c</sup> SEC (DMAc) number average molar mass in poly(MMA) equivalents. <sup>d</sup> Calculated molar mass (g mol<sup>-1</sup>) estimated using the relationship  $M_n(\text{calcd}) = ([M] \times \text{conv}) / ([\text{RAFT}] + (d \times 0.7 \times [\text{ACHN}] (1 - \exp(-k_d t))) \times M_{\text{monomer}} + M_{\text{RAFT}})$ , where  $d$  is assumed to be 1.0 for DMA, MA and St and 1.67 for MMA,  $k_d$  is the rate constant for decomposition of the initiator ( $9.59 \times 10^{-5} \text{ s}^{-1}$  at 100 °C and  $2.54 \times 10^{-5} \text{ s}^{-1}$  at 90 °C),  $t$  is the reaction time, and  $M_{\text{monomer}}$  and  $M_{\text{RAFT}}$  are the molar mass of the monomer and the RAFT agent, respectively. <sup>e</sup> Calculated end-group fidelity expressed as the fraction of living (dormant) ends,  $L = [\text{RAFT}] / ([\text{RAFT}] + (d \times 0.7 \times [\text{ACHN}] (1 - \exp(-k_d t))))$ . <sup>f</sup> Approximate transfer constant estimated using experimental  $M_n$  and  $\bar{D}$  (see Supporting Information). <sup>g</sup> SEC (THF) showed  $M_n$  14100  $\bar{D}$  1.55.

Table 2. RAFT copolymerizations in presence of 3,5-dimethyl-1H-pyrazole-1-carbodithioates **18-20**.<sup>a</sup>

monomer 1	monomer 2	[monomer] (M)	RAFT agent	[RAFT] (M)	[ACHN] <sup>b</sup> (M)	solvent <sup>b</sup>	time (h)	conv (%)	$M_n^c$	$M_n$ (calcd) <sup>d</sup>	$\bar{D}$	$L^e$
DMA		1.5	<b>18</b>	0.03	0.003	CH <sub>3</sub> CN	2	98	9600	8929	1.18	0.97
	MA	1.5						97				
DMA		1.5	<b>20</b>	0.03	0.003	CH <sub>3</sub> CN	2	97	9200	8967	1.13	0.97
	MA	1.5						98				
MMA		3.5	<b>20</b>	0.0263	0.0053	CH <sub>3</sub> CN	4	68	12000	8529	1.45	0.90
	DMA	0.0263						99				
MMA		1.75	<b>20</b>	0.0263	0.0053	CH <sub>3</sub> CN	4	91	13600	11631	1.18	0.90
	DMA	1.75						99				
MMA		1.5	<b>20</b>	0.03	0.006	Toluene	12	50	5100	4098	1.15	0.88
	St	1.5						36				
VAc		3.0	<b>18</b>	0.048	0.012	EtOAc	12	54	4700	2771	1.23	0.85
	DMA	0.048						99				
VAc		3.0	<b>19</b>	0.048	0.012	EtOAc	24	31	4200	1764	1.12	0.85
	DMA	0.048						99				
VAc		1.5	<b>18</b>	0.048	0.012	EtOAc	12	62	7600	4245	1.18	0.85
	DMA	1.5						99				
VAc		1.5	<b>20</b>	0.048	0.012	EtOAc	12	63	5300	4321	1.17	0.85
	DMA	1.5						99				
VAc		1.5	<b>20</b>	0.03	0.003	CH <sub>3</sub> CN	12	45	7900	6650	1.18	0.94
	DMA	1.5						99				

<sup>a</sup> All experiments were conducted with microwave heating at 100 °C. All concentrations are based on the mass or volume of material used at 22 °C and do not take into account volume of mixing effects. <sup>b</sup> ACHN = 1,1'-azobis(-1-cyanocyclohexane), EtOAc = ethyl acetate. <sup>c</sup> SEC (DMAc) number average molar mass in poly(MMA) equivalents. <sup>d</sup> Calculated molar mass (g mol<sup>-1</sup>) estimated using the relationship  $M_n(\text{calcd}) = (([M1] \times \text{conv1}) + [M2] \times \text{conv2}) / ([\text{RAFT}] + (d \times 0.7 \times [\text{ACHN}] (1 - \exp(k_d t))) \times M_{\text{monomers}} + M_{\text{RAFT}})$ , where [M1] is the concentration of monomer 1, [M2] is the concentration of monomer 2, conv1 and conv2 are the respective monomer conversions,  $d$  is assumed to be 1.0,  $k_d$  is the rate constant for decomposition of the initiator ( $9.59 \times 10^{-5} \text{ s}^{-1}$  at 100 °C),  $t$  is the reaction time, and  $M_{\text{monomer}}$  and  $M_{\text{RAFT}}$  are the molar mass of the RAFT agent, respectively. <sup>e</sup> Calculated end-group fidelity expressed as the fraction of living (dormant) ends,  $L = [\text{RAFT}] / ([\text{RAFT}] + (d \times 0.7 \times [\text{ACHN}] (1 - \exp(1 - \exp(k_d t))))$ .<sup>5</sup>

Table 3. Block copolymers prepared with 3,5-dimethyl-1H-pyrazole-1-carbodithioates **18** or **20**.<sup>a</sup>

monomer Block 1	monomer Block 2	[M] (M)	RAFT agent	[RAFT] (M)	[ACHN] <sup>b</sup> (M)	solvent	time (h)	conv (%)	$M_n^c$	$M_n$ (calcd) <sup>d</sup>	$\bar{D}$	$L^e$
DMA*		1.5	<b>18</b>	0.03	0.003	CH <sub>3</sub> CN	0.75	90	4600	5168	1.05	0.98
	MA (1:1) <sup>f</sup>	1.5						83				
DMA*		3.0	<b>18</b>	0.075	0.0015	CH <sub>3</sub> CN	0.87	85	4100	4424	1.07	0.99
	MA (5:1) <sup>f</sup>	3.0						85				
DMA*		1.5	<b>18</b>	0.03	0.003	CH <sub>3</sub> CN	1	98	5800	5168	1.05	0.98
	VAc (1:1) <sup>f</sup>	1.5						55				
DMA*		3.0	<b>18</b>	0.075	0.0015	CH <sub>3</sub> CN	0.87	85	4100	4424	1.07	0.99
	VAc (5:1) <sup>f</sup>	3.0						61				
DMA		1.5	<b>20</b>	0.03	0.003	CH <sub>3</sub> CN	0.75	86	5000	4474	1.07	0.98
	MA (1:1) <sup>f</sup>	1.5						86				
DMA*		1.5	<b>20</b>	0.03	0.003	CH <sub>3</sub> CN	0.75	92	5400	4771	1.07	0.98
	VAc (1:1) <sup>f</sup>	1.5						60				

<sup>a</sup> All experiments were conducted with microwave heating at 100 °C. All block copolymers were prepared as quasi-blocks by addition of the 2<sup>nd</sup> monomer and additional initiator and solvent to the polymerization reaction mixture without isolation of the 1<sup>st</sup> block. All concentrations are based on the mass or volume of material used at 22 °C and do not take into account volume of mixing effects. <sup>b</sup> ACHN = 1,1'-azobis[1-cyanocyclohexane]. <sup>c</sup> SEC (DMAc) number average molar mass in poly(MMA) equivalents. <sup>d</sup> Calculated molar mass (g mol<sup>-1</sup>) estimated using the relationship  $M_n(\text{calcd}) = ([M] \times \text{conv}) / ([\text{RAFT}] + (d \times 0.7 \times [\text{ACHN}] (1 - \exp(k_d t))) \times M_{\text{monomer}} + M_{\text{RAFT}})$ , where [M] is the total monomer concentration, [ACHN] is the initiator concentration (cumulative over both steps in the case of blocks),  $d$  is assumed to be 1.0,  $k_d$  is the rate constant for decomposition of the initiator ( $9.59 \times 10^{-5} \text{ s}^{-1}$  at 100 °C),  $t$  is the total reaction time, and  $M_{\text{monomer}}$  is the monomer molar mass (weighted average for copolymers), and  $M_{\text{RAFT}}$  is the molar mass of the RAFT agent or macro-RAFT, respectively. <sup>e</sup> Calculated end-group fidelity expressed as the fraction of living (dormant) ends,  $L = [\text{RAFT}] / ([\text{RAFT}] + (d \times 0.7 \times [\text{ACHN}] (1 - \exp(1 - \exp(k_d t))))$ .<sup>5</sup> <sup>f</sup> Ratio of monomer added in preparation of 2<sup>nd</sup> block to that used in preparation of 1<sup>st</sup> block.

## Experimental

### Materials and methods

The RAFT agents, benzyl 3,5-dimethyl-1H pyrazole-1-carbodithioate (**19**), and 2-cyanobutyl 3,5-dimethyl-1H pyrazole-1-carbodithioate (**20**), methyl 2-(((dodecylthio)carbonothioyl)thio)propanoate (**21**) and

cyanomethyl dodecyl carbonotrithioate (**22**) were prepared as indicated below or were obtained from Boron Molecular.<sup>62</sup> 3,5-Dimethylpyrazole was obtained from Fluka, chloroacetonitrile and benzyl chloride were obtained from Aldrich. Monomers (MA, DMA, St, MMA, VAc) were obtained from Aldrich and were treated with inhibitor remover (Aldrich) and flash-distilled immediately prior to use. ACHN (Vazo88™) was obtained from DuPont.

SEC (DMAc) was performed on a Shimadzu instrument equipped with a CMB-20A controller system, a SIL-20A HT autosampler, a LC-20AT tandem pump system, a DGU-20A degasser unit, a CTO-20AC column oven, a RDI-10A refractive index (RI) detector, and 4 × Styragel (Waters) columns (HT2, HT3, HT4 and HT5). *N,N*-dimethylacetamide (DMAc) (containing 4.3 g/L LiBr) was used as eluent at a flow rate of 1 mL/min. The column temperature was set to 80 °C and the RI detector temperature was set to 40 °C. The SEC was calibrated with low dispersity poly(MMA) standards, and molar mass are reported as poly(MMA) equivalents.  $M_n$  and  $\bar{D}$  were evaluated using Shimadzu software (LabSolutions version 5.63). A 3<sup>rd</sup> order polynomial was used to fit the log  $M$  vs. time calibration curve, which was approximately linear across the molar mass range of interest. SEC (THF) was performed was carried out with a Waters Associates liquid chromatograph equipped a Waters 2414 Refractive Index Detector and a Waters 2996 Photodiode Array Detector. Separations were achieved with a series of four Polymer Laboratories PLGel columns (3 × 5 μm Mixed-C and 1 × 3 μm Mixed-E) at 30 °C with solvent at 1 mL/min. The columns were calibrated with low dispersity polystyrene standards. The data were processed with Waters Empower Pro Software, a third order polynomial was used to fit the log<sub>10</sub> $M$  vs time calibration curve, which appeared approximately linear across the molar mass range  $2 \times 10^2 - 2 \times 10^6$  g mol<sup>-1</sup>.

Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance 400 (40 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C) or 500 spectrometer (500 MHz for <sup>1</sup>H). High resolution electron impact (HREI) mass spectra were performed on a Thermo Scientific Q Exactive™ mass spectrometer fitted with a HESI-II ion source. The solvent flow rate was 0.3 ml/min, the spray voltage was 3.0 kV and the capillary temperature was 300 °C. MALDI mass spectra were obtained with a Bruker Autoflex III smartbeam MALDI TOF-TOF operating in positive ion reflectron mode with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (usually known as DCTB) matrix (operating parameters are provided in the Supporting Information). UV-Vis spectra were recorded using a Hewlett Packard 8453 UV-spectrometer scanning between 200 and 800 nm. Microwave irradiation was carried out using a Biotage Initiator Sixty microwave system.

#### RAFT Agent Synthesis and Characterisation

**Potassium 3,5-dimethyl-1H-pyrazole-1-carbodithioate.** The salt was prepared according to procedure described in the literature.<sup>63</sup> To a solution of potassium hydroxide (6.16 g, 109.75 mmol, 1.06 equivalents) in tetrahydrofuran (100 mL) at 4 °C was added 3,5-dimethylpyrazole (10.00 g, 104.03 mmol).

The mixture was stirred at 4 °C for 5 min and carbon disulfide (8.17 mL, 10.30 g, 135.23 mmol, 1.3 equivalents) was then added slowly. The reaction mixture was stirred at 4 °C for 3 min and then at room temperature for 50 min. The mixture was filtered and the orange solid washed with diethyl ether and dried to yield the title compound as a light orange solid which was used in the next step without purification (19.52 g, 89%).

**Cyanomethyl 3,5-dimethyl-1H pyrazole-1-carbodithioate (18).** Potassium 3,5-dimethyl-1H-pyrazole-1-carbodithioate (18.60 g, 88.42 mmol) was dissolved in deionised water (350 mL) and then cooled in an ice-water bath. Chloroacetonitrile (5.92 mL, 7.01 g, 92.85 mmol, 1.05 equivalents) was then added and the reaction mixture was stirred in the ice-water bath for 2 min, and then at room temperature for 100 min. The mixture was then cooled in an ice-water bath for 15 min and filtered. The yellow solid was collected, washed with ice-cold water, and dried to give a first crop of product. The mother liquor was then stirred for 2 days, filtered and the yellow solid washed with ice-cold water and dried to give a second crop of product. The two crops were combined to give the product (**18**) as a pale yellow solid (11.49 g, 61%), m.p. 106.2 – 106.7 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 2.26 (s, 3H, CH<sub>3</sub>), 2.68 (d,  $J = 1.0$ Hz, 3H, CH<sub>3</sub>), 3.95 (s, 2H, CH<sub>2</sub>CN); 6.12 (d,  $J = 0.8$ Hz, 1H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 13.8, 17.2, 21.7, 114.2, 115.5, 146.3, 153.1, 195.4. HRMS (EI) Calculated for C<sub>8</sub>H<sub>10</sub>N<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup> 212.0311, Found 212.0317. UV – see Supporting Information.

**Benzyl 3,5-dimethyl-1H pyrazole-1-carbodithioate (19).** The title compound was prepared in a similar manner to that described for **18** except that benzyl chloride was used instead of chloroacetonitrile. The compound **19** was obtained in 59% yield as a yellow solid, m.p. 93.6 – 94.2 °C (lit. m.p. 75 °C,<sup>42</sup> 90–92 °C<sup>43,44</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 2.22 (s, 3H, CH<sub>3</sub>), 2.68 (d,  $J = 0.9$ Hz, 3H, CH<sub>3</sub>), 4.39 (s, 2H, CH<sub>2</sub>Ph), 6.06 (d,  $J = 0.6$ Hz, 1H, CH), 7.27 (m, 3H, ArH), 7.38 (m, 2H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 13.8, 17.6, 41.6, 113.5, 127.7, 128.7, 129.8, 135.0, 145.7, 152.0, 200.6. HRMS (EI) Calcd for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub> [M]<sup>+</sup> 262.0593, Found 262.0597. UV – see Supporting Information.

**2-cyano-2-butyl 3,5-dimethyl-1H pyrazole-1-carbodithioate (20).** The RAFT agent **20** was prepared by radical-induced decomposition of the bis(thioacyl) disulfide using a procedure analogous to that described in the literature<sup>45</sup> and had m.p. 114.4 – 115.0 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.20 (t  $J = 7.4$ Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.86 (s, 3H, CH<sub>3</sub>), 2.03 (m, 1H, CH<sub>2</sub>CH<sub>3</sub>), 2.24 (s, 3H, CH<sub>3</sub>), 2.27 (m, 1H, CH<sub>2</sub>CH<sub>3</sub>), 2.67 (d,  $J = 0.9$ Hz, 3H, CH<sub>3</sub>), 6.08 (d,  $J = 0.8$ Hz, 1H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 9.4, 13.8, 17.5, 24.0, 32.3, 46.4, 113.9, 120.0, 145.9, 152.0, 194.6. HRMS (EI) Calcd for C<sub>11</sub>H<sub>16</sub>N<sub>3</sub>S<sub>2</sub> [M+H]<sup>+</sup> 254.0780, Found 254.0788. UV – see Supporting Information.

#### Polymer Preparation

The monomer solutions prepared and were transferred to vials and degassed by nitrogen sparging for 15min. The vials were heated *via* microwave irradiation (Biotage Initiator Robot Sixty) at the specified temperature for the specified times. The percentage conversions were calculated from <sup>1</sup>H NMR spectra of the reaction mixtures using an internal standard (trioxane, 5

mg/mL). The following procedures are typical. All concentrations reported are based on amounts being additive and do not take into account any effects of volume of mixing or temperature.

**Preparation of poly(*N,N*-dimethyl acrylamide) using cyanomethyl 3,5-dimethyl-1*H* pyrazole-1-carbodithioate (**18**) at 100 °C.** A solution containing DMA (0.618 mL, 3 M), ACHN (2.93 mg, 0.006 M), **18** (12.68 mg, 0.03 M), trioxane (10mg; internal standard) and acetonitrile (1.382 mL) was prepared in a 5 mL microwave vial. The resulting mixture was degassed, sealed and heated at 100 °C by microwave irradiation for 1 h. The volatiles were removed *in vacuo* to give poly(DMA) at 99% conversion of DMA (determined by <sup>1</sup>H NMR), with  $M_n$  12,100,  $\bar{D}$  1.07 (refer entry 1 in Table 1).

**Preparation of poly(*N,N*-dimethylacrylamide)-co-poly(vinyl acetate) using cyanomethyl 3,5-dimethyl-1*H*-pyrazole-1-carbodithioate (**18**) at 100°C.** A solution containing DMA (0.010 mL, 0.048 M), VAc (0.553 mL, 3 M), ACHN (5.86 mg, 0.012 M), **18** (20.28 mg, 0.048 M), and ethyl acetate (1.437 mL) was prepared in a 5mL microwave vial. The resulting mixture was degassed, sealed and heated at 100 °C *via* microwave irradiation for 12 hours. The volatiles were removed *in vacuo* to give poly(DMA-co-VAc) at 55% conversion (>99% of DMA and 54% VAc), with  $M_n$  4,700,  $\bar{D}$  1.23 (refer entry 5 in Table 2).

**Preparation of poly(*N,N*-dimethylacrylamide)-block-poly(vinyl acetate) using cyanomethyl 3,5-dimethyl-1*H*-pyrazole-1-carbodithioate (**18**) at 100°C.** A solution containing DMA (0.309 mL, 1.5 M), ACHN (1.47 mg, 0.003 M), cyanomethyl **18** (12.68 mg, 0.03 M) in acetonitrile was prepared in a 5mL microwave vial. The resulting mixture was degassed, sealed and heated at 100 °C *via* microwave irradiation for 1 h (a sample showed poly(DMA) at 98% conversion with  $M_n$  5,800,  $\bar{D}$  1.05). The vial cap was removed and VAc (0.553mL) and ACHN (1.47 mg) was added. The vial was again sealed, degassed and heated at 100 °C *via* microwave irradiation for 24 hours. The volatiles were removed *in vacuo* to give poly(DMA)-block-poly(VAc) at >99 % conversion of DMA and 55% conversion of VAc, with  $M_n$  8500,  $\bar{D}$  1.24 (refer entry 3 in Table 3).

#### DOSY NMR

Samples for NMR diffusion measurements were prepared by dissolving approx. 8 mg of polymer with 0.6 ml of methanol-*d*<sub>4</sub>. NMR diffusion coefficients were determined using the pulsed field gradients spin echo method utilising a Bruker Av500 NMR spectrometer equipped with a 5 mm Bruker CryoProbe Prodigy H/F-C/N-D probe operating at 500.13 MHz for <sup>1</sup>H with a 6.6 G/mm z-gradient. Samples were maintained at 25°C and at least 30 min was allowed for each sample to thermally equilibrate before any measurements were made. The diffusion coefficients were measured with a stimulated echo sequence with one spoil gradient. The diffusion time ( $\Delta$ ) and the gradient pulse length ( $\delta$ ) were optimised for each sample;  $\Delta$  was 50 ms while  $\delta$  was 3 ms (DMA precursor) or 5 ms (MA-b-DMA). Gradient pulses were smoothed square chirp shape. Experiments were performed as pseudo-2D with a linear variation of the gradient from 2 to 95% of maximum intensity

in 32 steps. The data were processed and the peak areas were used to fit the equation  $I = I_0 e^{-D(2\pi\gamma\delta)^2[(\Delta-\delta)/3]\times 10^4}$  to determine the diffusion coefficient, *D*. The spectra are provided in Figure 9.

## Conclusions

3,5-Dimethyl-1*H*-pyrazole-1-carbodithioates (**18-20**) have been shown to have wide-spread applicability, able to control the polymerizations of both MAMs (MA, DMA, MMA and St) and a LAM (VAc). End group fidelity was proved with the synthesis of block copolymers. The ability to control polymerization of both MAMs and LAMs renders these RAFT agents suitable for the synthesis of poly(MAM)-block-poly(LAM). The RAFT agents are an appropriate replacement for trithiocarbonate RAFT agents in most circumstances and have the distinct advantage that the derived polymers do not develop odour on storage (no low molar mass thiols are generated).

The RAFT agents **18-20** can be seen as superior to the switchable RAFT agents **10/10H**<sup>+</sup> with similar 'R' in that **18-20** can be applied to both mediate the polymerization of both MAMs and LAMs and no switching process is required. The disadvantage of **18-20** is the significant retardation that is evident when they are used to control the polymerization of LAMs (VAc). The factors causing slow polymerization can also be judged responsible for the pre-tailing and relatively high dispersities observed for poly(DMA)-block-poly(VAc) formed using **18**. Thus, the switchable RAFT agents remain preferred when low dispersity poly(MAM)-block-poly(LAM) are required.

Studies are currently underway to more fully explore the scope and versatility of the 1*H*-pyrazole-1-carbodithioates RAFT agents.

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## Dithiocarbamate RAFT agents with broad applicability – the 3,5-Dimethyl-1*H*-pyrazole-1-carbodithioates

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The RAFT agents offer  $D < 1.1$  for MAMs, methyl acrylate (MA), *N,N*-dimethylacrylamide (DMA) and styrene, and  $D < 1.3$  for LAMs, vinyl acetate (VAc); versatility and end-group fidelity was proved with synthesis both polyDMA-*block*-polyMA and polyDMA-*block*-polyVAc.

