

**Tailoring Polymer Dispersity by Mixing Chain Transfer  
Agents in PET-RAFT Polymerization**

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## COMMUNICATION

## Tailoring Polymer Dispersity by Mixing Chain Transfer Agents in PET-RAFT Polymerization

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**Here we report a simple and versatile batch methodology to tailor polymer dispersity utilizing PET-RAFT polymerization. By mixing two chain transfer agents (CTAs) possessing different transfer constant (a higher and a lower transfer constant CTA) in different ratios, control over the dispersity ( $\mathcal{D} = 1.08\text{--}1.82$ ) can be achieved for a range of monomer classes including methacrylates, acrylates and acrylamides while maintaining monomodal molecular weight distributions. High end-group fidelity of both low and high dispersity macroCTAs were confirmed by the synthesis of block copolymers. In contrast to previously developed photo-mediated methodologies, we show that PET-RAFT exhibits perfect temporal control for all targeted dispersities regardless of the percentage of the lower transfer constant CTA employed. Other benefits of the approach include the use of visible light irradiation, ppm concentrations of a photo-redox catalyst and the possibility to manipulate  $\mathcal{D}$  in the absence of external deoxygenation methodologies, which significantly simplifies the process.**

Reversible deactivation radical polymerization (RDRP) has significantly contributed to the evolution of modern polymer chemistry by providing access to a range of polymeric materials with controlled molecular weight, architecture, functionality and dispersity ( $\mathcal{D}$ ) from a range of functional groups.<sup>1–4</sup> In particular,  $\mathcal{D}$  (as a measure of the breath of the molecular weight distribution) is an important parameter to control as it determines the polymer properties.<sup>5, 6</sup> For many years, the main target of RDRP methodologies was the synthesis of low  $\mathcal{D}$  polymers while materials of higher  $\mathcal{D}$  were considered less desirable and often associated with low livingness.<sup>7</sup> However, a number of studies have recently revealed that both low and high  $\mathcal{D}$  polymers possess

interesting and complementary properties and as such developing new strategies to tailor molecular weight distributions, is highly desirable and a current challenge in polymer chemistry.<sup>8, 9</sup> The traditional method to tune polymer dispersity is by blending pre-synthesized polymers of different molecular weights.<sup>10–13</sup> Despite the simplicity of this method and the possibility to obtain a wide range of  $\mathcal{D}$ s, it can be time-consuming and often leads to multimodal molecular weight distributions. In 2016, Fors and co-workers reported an elegant engineering approach to tune molecular weight distributions, whereby the relative rate of initiation to propagation was controlled through the gradual feeding of an initiator during the nitroxide mediated polymerization of styrene yielding materials with various  $\mathcal{D}$ s.<sup>14–16</sup> The same approach was also successfully applied to anionic polymerization.<sup>17</sup> In an alternative methodology, Boyer, Xu and co-workers cleverly controlled the molecular weight distributions through flow polymerization by carefully adjusting flow rates, chemical compositions and residence times.<sup>18, 19</sup> More recently, Goto's group developed an innovative temperature selective method where different amounts of butyl acrylate were added during the reversible complexation mediated polymerization of methyl methacrylate, achieving good control over the dispersity of a range of architectures.<sup>20</sup> In another report, Matyjaszewski and co-workers efficiently tuned the catalyst concentration in atom transfer radical polymerization (ATRP) to afford polymers with tailored  $\mathcal{D}$ s.<sup>21</sup> Other examples to tailor polymer dispersity include the use of reducing agents, photochromic initiators, flow chemistry and termination agents.<sup>22–26</sup> Despite the well-recognized benefits of utilizing light as an external stimulus (*e.g.* widely available, non-invasive *etc.*),<sup>27–30</sup> perfect temporal control for a wide range of targeted  $\mathcal{D}$ s has not been demonstrated by any photo-polymerization method.<sup>31–34</sup> For instance, in photo-ATRP, complete cessation of the polymerization in the absence of light

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Electronic Supplementary Information (ESI) available: [Experimental procedures, detailed polymerization results, SEC and NMR data are included].

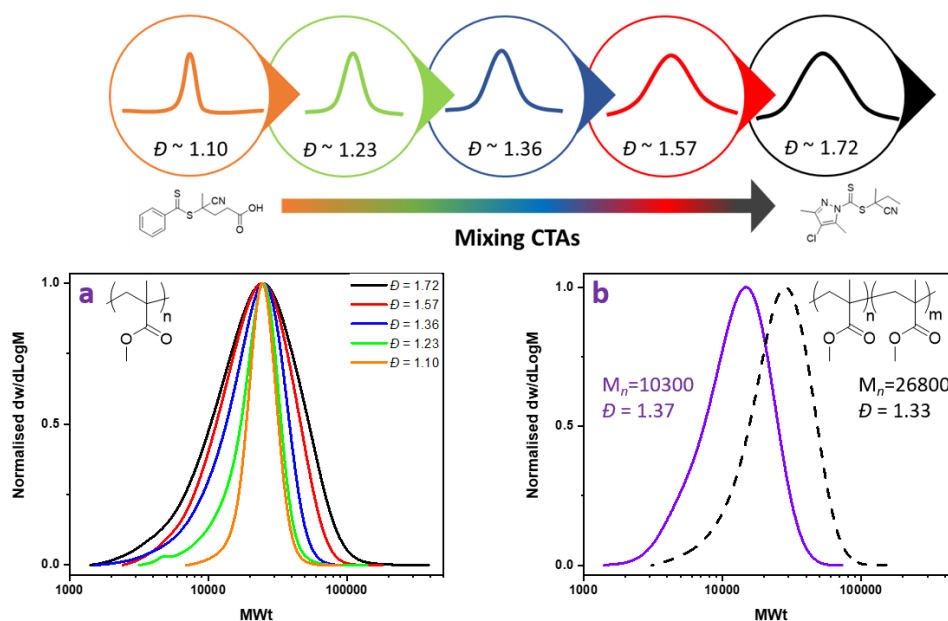
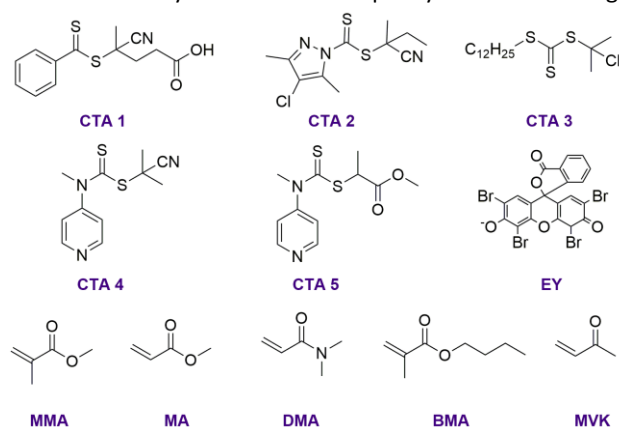


Figure 1: SEC analysis of the polymerization of MMA, illustrating a) the variation in dispersity as CTA 1 and CTA 2 are mixed in different ratios (aligned by  $M_p$  value) and b) a chain extension of a PMMA macroCTA prepared with 10 % CTA 1 and 90 % CTA 2 with MMA.

irradiation could only be achieved for very high dispersity values ( $\bar{D} \sim 1.80$ ) while for lower and intermediate  $\bar{D}$ s imperfect temporal control was reported.<sup>32, 35</sup> RAFT on the other side, can exhibit perfect temporal control for low  $\bar{D}$ s but the technique's capability to maintain excellent temporal control for intermediate and high  $\bar{D}$ s has not been explored. In addition, broadening the molecular weight distributions often leads to a disagreement between theoretical and experimental molecular weight, which has been attributed to slow initiation in ATRP.<sup>32</sup> It is also noted that in many methods, multimodal molecular weight distributions and low end-group fidelity compromise the potential applications of the resulting materials.<sup>25, 36</sup> Last but not least, the vast majority of reported strategies require tedious external deoxygenation, *e.g.* freeze-pump-thaw cycles, nitrogen bubbling, *etc.* We envisaged that we could address many of the aforementioned issues by combining the benefits of photoinduced electron transfer reversible addition-fragmentation chain transfer (PET-RAFT) polymerization with a recent publication from our group where traditional thermal RAFT polymerization was employed to tailor polymer  $\bar{D}$ s by mixing different chain transfer agents.<sup>37</sup> Key to this mixing approach is the selection of two suitable CTAs with different transfer constants, of which the higher transfer constant one would afford polymers with low  $\bar{D}$  and the lower transfer constant would lead to broader molecular weight distributions. The two selected CTAs would be then mixed in various ratios to allow the synthesis of polymers exhibiting a wide range of  $\bar{D}$ s. If successful, our work would represent the first example of a batch PET-RAFT methodology where polymer  $\bar{D}$  can be tailored upon demand. Additional benefits would arise from the possibility to achieve perfect temporal control for any targeted dispersity, the use of visible light irradiation and ppm concentrations of catalyst as well as the opportunity to conduct the reactions in the absence of any external deoxygenation. It is noted that our mixed RAFT

agent system is fundamentally different than the mixed ligand system previously employed by Percec and co-workers in copper-mediated polymerizations where an acceleration of the polymerization rate was observed (rather than a change in the attained dispersity).<sup>38, 39</sup> A list of all reagents employed in this study are summarized in Scheme 1. To explore the possibility of PET-RAFT polymerization to tailor polymer dispersity in batch, methyl methacrylate (MMA) was used as a model monomer, Eosin Y (EY) as a photo-redox catalyst and DMSO as a solvent, following the pioneering work by Boyer and co-workers, using blue light LED irradiation (12 W,  $\lambda_{\max} = 465 \pm 5$  nm) in a homemade box (Fig. S1).<sup>40, 41</sup> 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTA 1) was selected as a high transfer constant CTA (Scheme 1), because it is a widely used CTA to polymerize methacrylic monomers owing to the stabilization of the intermediate radical offered by the phenyl Z group.



Scheme 1: Summary of reagents employed in this study.

Indeed, polymerization of MMA under the aforementioned conditions, led to well-defined PMMA with narrow molecular

weight distributions ( $\mathcal{D} \sim 1.10$ ,  $M_n = 22700$ ) (Fig. 1a, Table S1 Entry 5). Instead, the selection of the low transfer constant CTA is much more challenging. To select a suitably low transfer constant CTA, the following three main criteria were considered. Firstly, the chosen CTA should allow for the synthesis of polymers of sufficiently high  $\mathcal{D}$  ( $> 1.5$  to resemble values typically obtained during free radical polymerization). Secondly, it should allow monomodal molecular weight distributions to be targeted while maintaining high livingness. Last but not least, an “ideal” low transfer constant CTA should not compromise the agreement between theoretical and experimental molecular weights or lead to slow polymerization. To satisfy these requirements, 2-Cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate (CTA 2) was selected as the low transfer constant CTA. By using CTA 2 to polymerize MMA, fairly broad, yet monomodal, molecular weight distributions were obtained ( $\mathcal{D} \sim 1.72$ ) (Fig. 1a, Table S1 Entry 1). By varying the ratio between CTA 1 and CTA 2, any intermediate  $\mathcal{D}$  could be obtained ( $\mathcal{D} \sim 1.08$ - $1.72$ ) (Fig. 1a and Fig. S2, Table S1 and S2). For instance, when 70 % of high transfer constant CTA 1 and 30 % of low transfer constant CTA 2 were mixed, a dispersity of 1.23 could be attained. To target higher dispersity values, the amount of CTA 2 was increased to 60 % and 90 %, yielding  $\mathcal{D} \sim 1.36$  and  $\mathcal{D} \sim 1.57$  respectively (Fig. 1a, Table S1, Entries 2-3). Importantly, similar dispersity values could be attained in different monomer concentrations (1:1, 1:3, 1:5 and 1:10 monomer to solvent) (Fig. S3). These initial experiments demonstrate that by simply mixing 2 commercially available CTAs, polymers with a range of  $\mathcal{D}$ s can be synthesized through PET-RAFT polymerization. The livingness of the synthesized materials was subsequently investigated. Upon addition of a second aliquot of MMA, efficient chain extensions could be performed. In particular, a macroCTA with an intermediate dispersity ( $\mathcal{D} = 1.37$ ,  $M_n = 10300$ ) was successfully chain extended reaching higher molecular weights ( $M_n = 26800$ ) and maintaining a relatively constant dispersity ( $\mathcal{D} = 1.33$ ) (Fig. 1b and Fig. S4 and S5). *In-situ* chain extension from the highest dispersity PMMA synthesized through the exclusive use of CTA 2 was also possible (Fig. S6). Importantly, in all cases fairly good agreement between experimental and theoretical molecular weights could be maintained (Table S1 and S2). The preparation of block copolymers was also possible. Starting from a PMMA with  $\mathcal{D} = 1.37$  ( $M_n = 10300$ ), a well-defined P(MMA-*b*-BMA) could be synthesized with the molecular weight distributions shifting clearly to higher molecular weights ( $M_n = 21400$ ,  $\mathcal{D} \sim 1.35$ ) (Fig. 2a and Fig. S7). In a similar vein, a high dispersity PMMA ( $\mathcal{D} \sim 1.64$ ) could be efficiently chain extended *in-situ* with methyl vinyl ketone (MVK) yielding a block copolymer with final dispersity of 1.50 (Fig. 2b and Fig. S8). These results highlight that high livingness can be maintained regardless of the initial dispersity of the macroCTA.

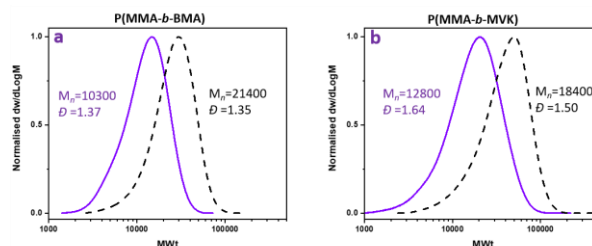


Figure 2: SEC analysis of block copolymers formed from a) mixed CTAs P(MMA-*b*-PBMA) and b) only CTA 2 P(MMA-*b*-PMVK).

One significant advantage of PET-RAFT polymerization is the use of visible light as a stimulus to initiate and mediate the polymerization. To investigate the possibility of temporal control in our system, “on-off” experiments were designed and special emphasis was given to long “off” periods (*i.e.*  $> 10$  h) to ensure accuracy and to eliminate experimental error.<sup>42</sup> When targeting intermediate dispersities (CTA 1: CTA 2  $\sim$  35: 65,  $\mathcal{D} = 1.24$ - $1.33$ ), our kinetics showed that  $M_n$  grows linearly with conversion and the polymerization can completely cease during the dark periods (Fig. 3a,c). This is in contrast to photo-ATRP where cessation of polymerization was only possible at extremely high  $\mathcal{D}$ s while for lower and intermediate  $\mathcal{D}$ s, the reaction continued in the absence of light irradiation, albeit at a slower rate.<sup>32, 35</sup> In addition, when targeting higher  $\mathcal{D}$ s through our approach (CTA 2 only  $\mathcal{D} = 1.64$ - $1.72$ ), a non-linear molecular weight evolution was observed with the  $M_n$  reaching relatively high values at low conversion (Fig. 3d). Significantly, complete cessation of the polymerization during the “off” periods could also be achieved when only CTA 2 was employed (Fig. 3b), thus demonstrating that PET-RAFT offers excellent temporal control for the entire range of targeted  $\mathcal{D}$ s. To the best of our knowledge, this is the first example where perfect temporal has been demonstrated for any targeted dispersity.

Oxygen-tolerant polymerizations have recently received considerable attention as they eliminate the laborious task of conventional deoxygenation, (*e.g.* freeze pump-thaw-cycles, nitrogen bubbling, *etc.*) offering an inexpensive, fast and simple way to synthesize polymers without requiring a complex set-up or extensive training.<sup>43-47</sup> In our previous investigation to tune polymer  $\mathcal{D}$  all experiments were conducted under strict deoxygenation conditions using thermal RAFT polymerization.<sup>37</sup> However, PET-RAFT offers the opportunity for the polymerizations to proceed without the need for external deoxygenation. Indeed, a range of different  $\mathcal{D}$  of PMMAs could be obtained by using mixtures of CTA 1 and CTA 2 in the absence of any external deoxygenation when headspace was minimised to reduce the amount of oxygen present in the reaction vessel (Fig. S9 and Table S3). It is highlighted that oxygen-tolerant polymerizations usually operated in an ideal fashion when using DMSO as the solvent.<sup>46</sup>

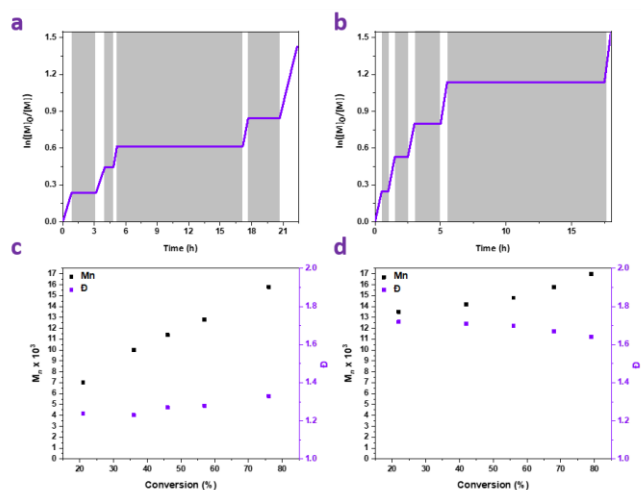


Figure 3: "ON/OFF" study for PET-RAFT polymerization of MMA: (a)  $\ln([M]_0/[M]_t)$  vs. time of exposure, CTA 1: CTA 2 ratio 35: 65 % (b)  $\ln([M]_0/[M]_t)$  vs. time of exposure, only CTA 2 (c) molecular weights and  $M_w/M_n$  vs. conversion, CTA 1: CTA 2 ratio 35: 65 % (d) molecular weights and  $M_w/M_n$  vs. conversion, only CTA 2.

To examine the compatibility of our strategy with other monomer classes, we selected methyl acrylate (MA) as the next model monomer. Due to the change in monomer activity, a different pair of CTAs was selected. As the high transfer constant CTA, 2-cyano-2-propyl dodecyl trithiocarbonate (CTA 3) was chosen, yielding PMA with  $\bar{D} \sim 1.11$  ( $M_n = 23400$ ) (Fig. 4a and Table S4 Entry 5). 2-cyanopropan-2-yl N-methyl-N-(pyridin-4-yl)carbamodithioate (CTA 4) was utilized as the low transfer constant CTA allowing much broader molecular weight distributions to be obtained ( $\bar{D} \sim 1.52$ , Fig. 4a and Table S4 Entry 1). By mixing CTA 3 with CTA 4 in different ratios, any intermediate  $\bar{D}$  could be targeted while ensuring monomodal distributions and good agreement between theoretical and experimental molecular weights (Fig. 4a and Table S4). Our strategy was finally extended to acrylamides, where dimethyl acrylamide (DMA) could be polymerized successfully yielding various intermediate  $\bar{D}$ s upon mixing CTA 3 ( $\bar{D} \sim 1.10$ ) with methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate (CTA 5) ( $\bar{D} \sim 1.82$ ) (Fig. 4b and Table S5). Thus, our methodology demonstrated excellent compatibility with different polymer classes.

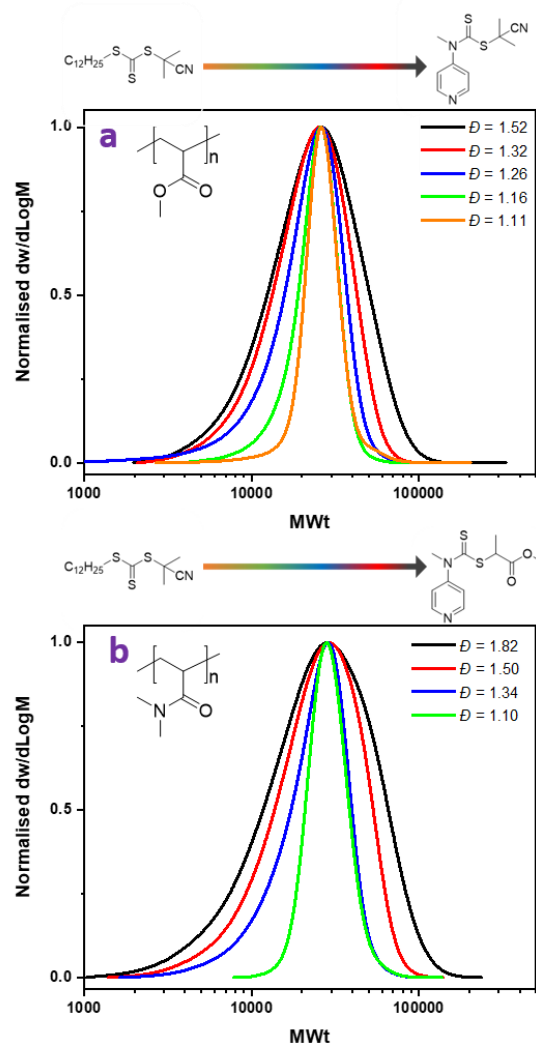


Figure 4: SEC analysis of the polymerization of a) methyl acrylate (CTAs 3 and 4 mixed) and b) dimethyl acrylamide (CTAs 3 and 5 were mixed) illustrating the variation in dispersity as two CTAs are mixed in different ratios (aligned by  $M_p$  value).

In summary, we reported the first example of a batch PET-RAFT polymerization methodology where excellent temporal control can be achieved for a wide range of targeted  $\bar{D}$ s. By mixing two CTAs of different transfer constants, tuneable dispersities ( $\bar{D} \sim 1.08$ -1.82) can be attained while maintaining monomodal molecular weight distributions, good agreement between experimental and theoretical molecular weights and high livingness. The high end-group fidelity was verified through chain extensions and block copolymers yielding well-defined polymeric materials. The developed approach could also be performed in the absence of any external deoxygenation method, thus significantly simplifying the process and expanding the chemical toolbox for tuning polymer dispersity.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgments

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## Author Contributions

‡ These authors contributed equally to the work.

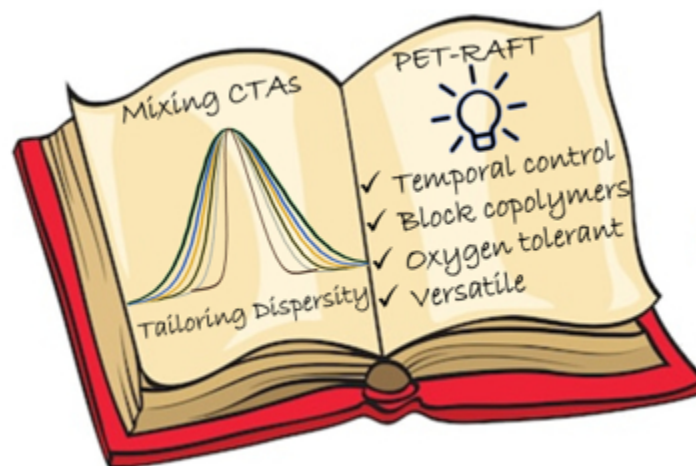
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