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Controlling polymer dispersity using switchable RAFT agents: Unravelling the effect of the organic content and degree of polymerization

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ABSTRACT

Dispersity can significantly affect material properties and related applications and as such is a significant parameter to control in polymer design. Switchable RAFT agents were recently utilized as an efficient tool to tailor polymer dispersity. In this work, we investigate the effect of the organic solvent and targeted degree of polymerization (DP) in attaining dispersity-controlled homopolymers and block copolymers. By varying the addition of acid in pure aqueous media we found that a dispersity range between 1.16 and 1.58 could be obtained while the gradual incorporation of the organic content led to broader dispersity ranges. Pleasingly, when the polymerizations were performed in aqueous media, dispersity could be efficiently controlled regardless of the targeted degree of polymerization (from DP 50 to DP 800). Instead, in mixtures containing [DMF]:[H_2O] = 4:1, dispersity could be successfully tailored only up to DP = 200 while for higher targeted DPs, a reduction in the final dispersity was not feasible. To expand the scope of our system, we subsequently exploited alternative organic solvents including DMAc, dioxane, DMSO, and ACN. While DMAc showed a side reaction attributed to the high amounts of acid employed, the other solvents successfully resulted in an efficient control over dispersity with ACN requiring the lowest amount of acid to achieve the lowest dispersity value (i.e. 2 equivalents of acid yielded $Đ \sim 1.19$). Notably, the highest $Đ$ polymers synthesized in the various solvents displayed very high end-group fidelity as characterized by mass-spectrometry and *in-situ* chain extensions. After establishing optimal reaction conditions, we also synthesized a range of exemplary diblock and triblock copolymers (with alternating low and high $Đ$) demonstrating excellent dispersity control upon subsequent block additions.

1. Introduction

Controlled radical polymerization methods enable the synthesis of polymers with controlled molecular weight, architecture, end-group fidelity and dispersity.[1–10] For years, polymers exhibiting high livingness were considered to intrinsically also possess low dispersity values and *vice versa* following a common misconception that broad molar mass distributions must be associated with increased side reactions. However, it has recently become evident that these two terms should not be related and high dispersity polymers can also display very high-end group fidelity.[11–14] Considering that both low and high dispersity polymers can be advantageous for a wide range of applications[7,10,15–17] many groups have exploited engineering and chemistry approaches to control dispersity as well as the shape of molar mass distributions.[12,18–28] Polymer blending, for example, is a traditional way to control polymer dispersity by synthesizing a range of polymers (e.g. 10–20 polymers) with different molecular weights and mixing them.[23,29,30] Although this methodology usually results in bimodal molar mass distributions, our group recently demonstrated that by simply mixing two polymers (one of high $Đ$ and one of low $Đ$), any intermediate dispersity value could be obtained with extremely high precision.[31] In 2016, Fors and co-workers introduced an exciting approach whereby the shape of the molar mass distributions could be efficiently controlled by leveraging the temporal regulation of initiation.[32,33] In particular, a syringe pump was utilized to gradually feed the initiating species in an already ongoing controlled polymerization resulting in shape-controlled distributions.[17,22,34,35] In an alternative strategy, Guironnet's group subsequently employed a computer-controlled tubular flow reactor providing a general route to designing polymer molar mass distributions through flow chemistry.[36] Boyer and co-workers also contributed to this direction by elegantly combining flow-mediated polymerization approaches with mathematical models to fully control the shape of molar mass distributions.[37–39]

Chemistry strategies have also been developed to control polymer

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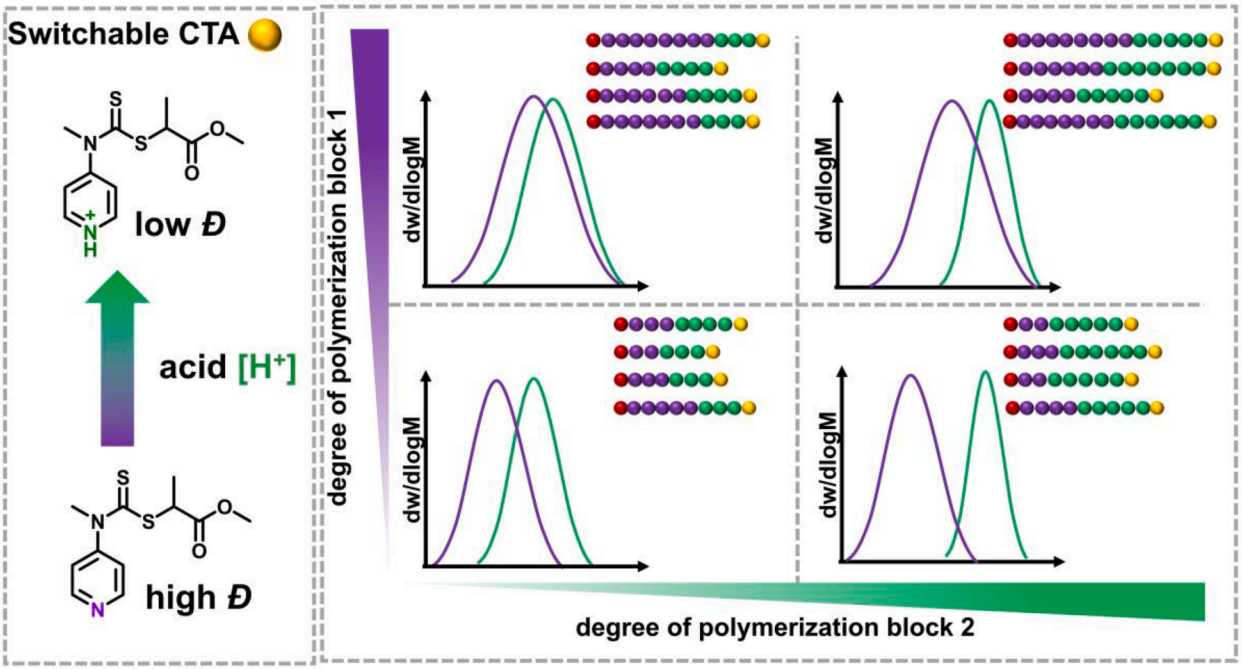

Fig. 1. Tuning dispersity in block copolymers using a switchable RAFT agent.

dispersity by manipulating important polymerization steps such as initiation and/or deactivation.[11,12,24,40,41] Such methods offer additional opportunities when compared to engineering alternatives as they often result in fairly monomodal molar mass distributions, do not require any specialized equipment (e.g. syringe pumps or specialized software), and are quite simple to implement. For instance, Matyjaszewski and coworkers and our group independently regulated the deactivation step in atom transfer radical polymerization (ATRP) by simply varying the copper or iron catalyst concentration yielding homopolymers with a wide range of dispersities and without compromising their end-group fidelity.[42–46] As the ATRP methods are rather limited in monomer scope[44,47], our group developed a straightforward batch reversible addition-fragmentation chain-transfer (RAFT) polymerization method to tailor polymer dispersity for a range of monomer classes including (meth) acrylates, acrylamides and styrene as well as methacrylic acid, methyl vinyl ketone and vinyl acetate. This was

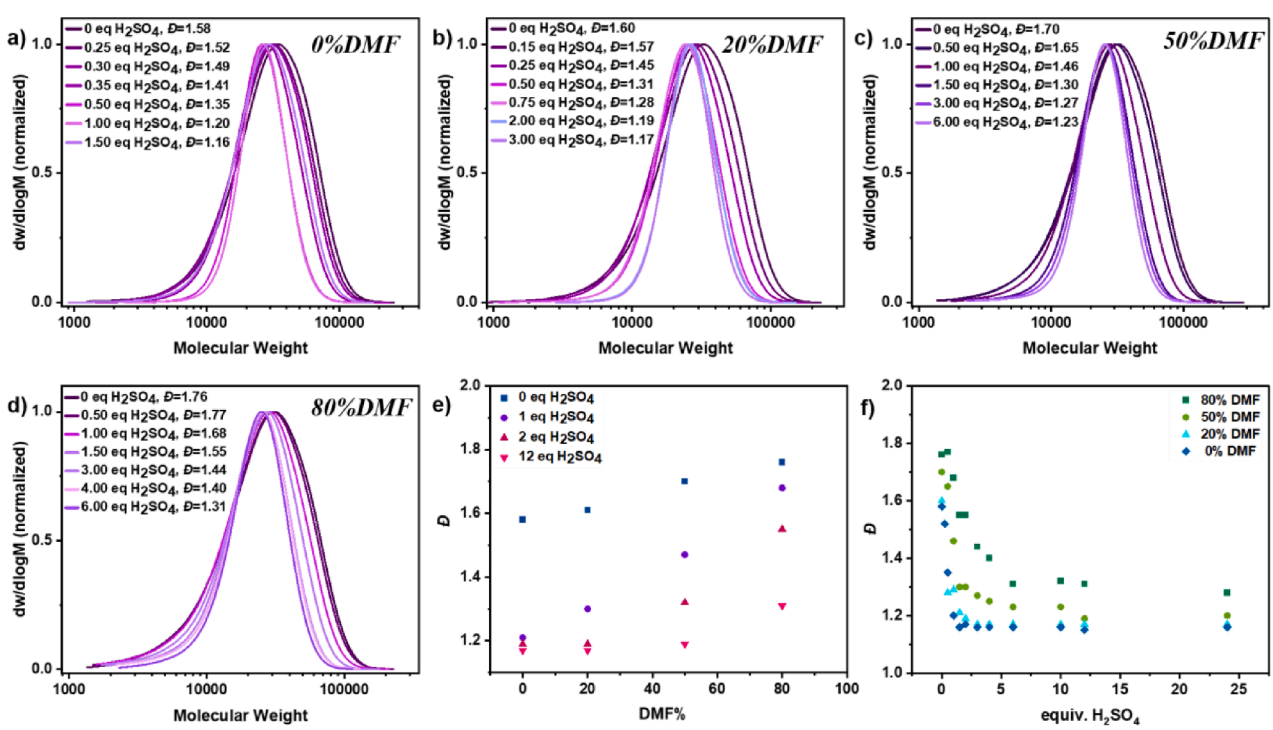

Fig. 2. The effect of varying the organic content concentration in the RAFT polymerization of DMA. SEC traces illustrate syntheses with various amounts of acid a) in the absence of organic solvent, b) with 20% organic solvent, c) with 50% organic solvent and d) with 80% organic solvent. Scatter plots illustrate the overall trends with dispersity changes plotted against e) organic content and f) acid concentration.

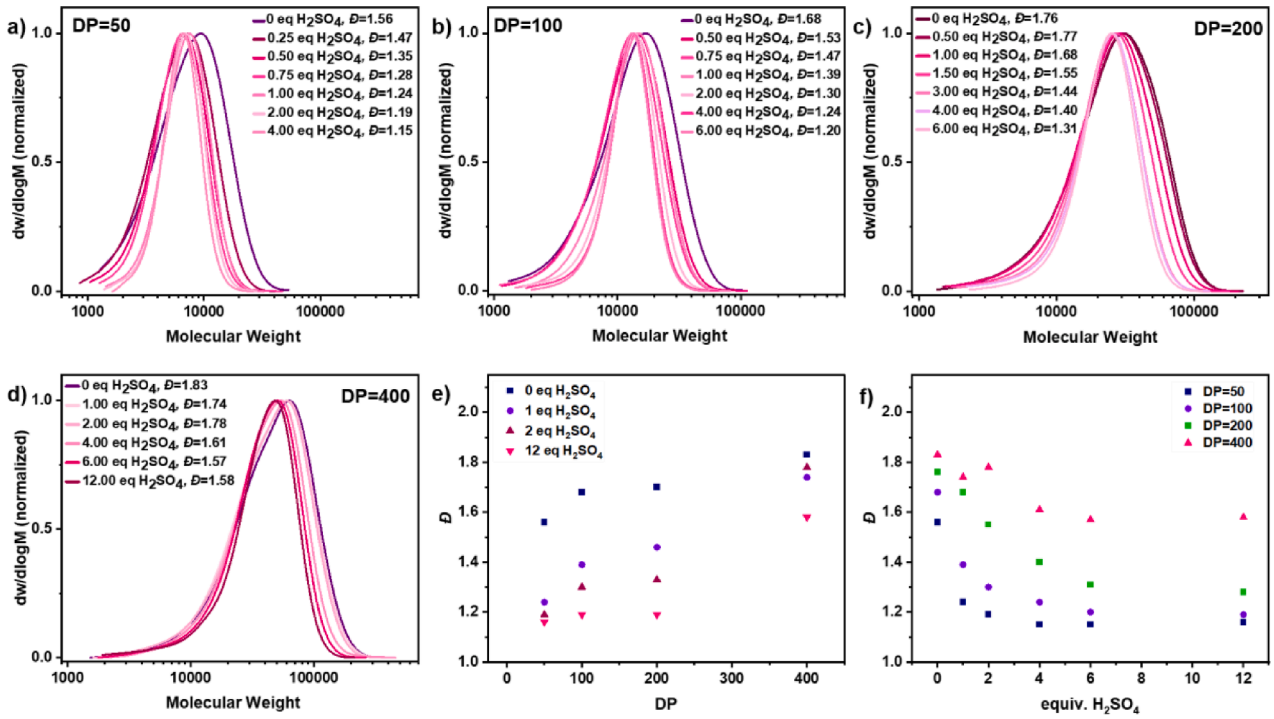

Fig. 3. The effect of acid concentration on dispersity at various degrees of polymerization. SEC traces illustrate syntheses with various amounts of acid for a) DP50, b) DP100, c) DP200 and d) DP400. Scatter plots illustrate the overall trends with dispersity changes plotted against e) target DP and f) acid concentration. All reactions were performed in 80% organic media.

achieved by mixing two RAFT agents with vastly different chain transfer constants in various ratios.[24,25]

Several other chemistry approaches have also been developed including Goto's work in exploiting a small amount of a co-monomer during reversible complexation-mediated polymerization[13] and Chiu's work on utilizing photochromic initiators in cationic polymerization.[14] One common limitation of many of the aforementioned methodologies is the challenge of achieving dispersity control in block copolymers and multiblock copolymers.[48–52] Our group was able to circumvent this by recently reporting the synthesis of sequence-controlled multiblocks with on-demand control over dispersity.[53] The key to our approach was the regulation of the activity of the chain transfer agent during RAFT polymerization. In particular, we leveraged a switchable RAFT agent, also referred to as a universal RAFT agent [54–56], allowing access to dispersity control in both homopolymers and multiblock copolymers while also achieving near-quantitative yields and very high livingness.[53] However, the effect of the organic solvent and the degree of polymerization on the final dispersity has yet to be investigated, limiting the scope of our approach (Fig. 1).

2. Results and discussion

2.1. Effect of increasing the organic content concentration

For the initial experiments, methyl 2-[methyl(4-pyridinyl) carbamothioylthio]propionate was used as the switchable RAFT agent, dimethylacrylamide (DMA) as a model monomer, 2-2′-azobis[2-(2-imidazoline-2-yl)propane] dichloride (VA-044) as the free radical initiator and dimethylformamide (DMF) as the organic solvent. Although depending on the organic content, a different amount of VA-044 is required to achieve quantitative monomer conversion (Figure S1) (i.e. the higher the water content the less free radical initiator is needed [51,57]), we consistently employed 0.1 equivalents with respect to the RAFT agent for all polymerizations to allow for a more meaningful comparison. The targeted degree of polymerization (DP) was set at 200 and the monomer concentration was fixed at 20 v/v.

Under the aforementioned conditions, the first polymerization was conducted in pure aqueous media and in the absence of added acid, (i.e. sulphuric acid) a broad, yet monomodal, molar mass distribution (M_n = 23,400, Đ=1.58) was obtained with good agreement between theoretical and experimental molecular weight (Fig. 2a). A near-quantitative conversion was reached within 2 h as evident by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and the chain transfer agent was fully consumed according to the size exclusion chromatography (SEC) UV-detector (Figure S2). Upon replicating the experiment, albeit with 0.25 equivalents of sulphuric acid, the dispersity was decreased to 1.52, while further increases in the amount of added acid (0.5, 1 and 1.5 equivalents) led to gradually lower Đs (1.35, 1.20 and 1.16, respectively, Fig. 2a, Table S1). It is noted that a slight excess of acid was required to fully protonate the RAFT agent and reach the minimum Đ value due to the presence of DMA which elevates the initial pH value to approximately 9–10 (prior to the addition of acid).[55,58]

Switching from aqueous media to a mixture of [DMF]:[H_2O] = 1:4 led to comparable data, although a higher excess of acid (i.e. 3 equivalents) was required to attain the lowest possible Đ (Fig. 2b, Table S2). Instead, when the polymerizations were performed in mixtures of [DMF]:[H_2O] = 1:1, a higher Đ (~1.70) could be obtained when the deprotonated RAFT agent was utilized (Fig. 2c, Table S3). As such, a broader Đ range was possible under these conditions (1.23–1.70), thus highlighting an advantage of employing formulations with increased organic content. However, when the DMF percentage was increased further ([DMF]:[H_2O] = 4:1), the lowest Đ that could be achieved was 1.31 (6 equivalents of acid) and no further decrease was possible regardless of the amount of added acid (e.g. up to 12 equivalents, Fig. 2d-f, Table S4). Nevertheless, by increasing the organic content we pave the way for the potential control over the Đ of more hydrophobic monomers, thus significantly expanding the scope of the developed system. It is noted that for all the higher Đs attained, successful *in-situ* chain-extension experiments were conducted, revealing that very high livingness could be maintained (see section entitled effect of various

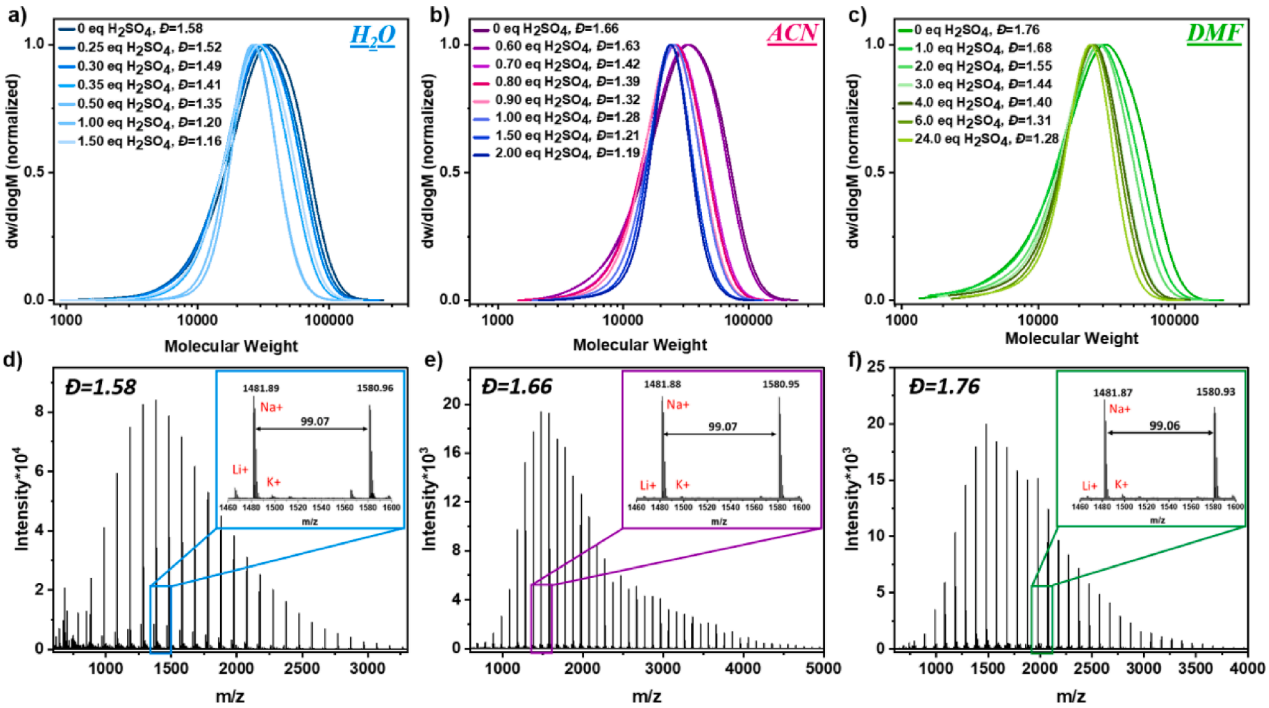

Fig. 4. The effect of solvent choice on the dispersity of homopolymers at various acid concentrations. SEC traces illustrate syntheses of DP200 in a) 100% water, b) 80:20 ACN: water and c) 80:20 DMF: water. The analogous MALDI-ToF-MS data illustrates the results for homopolymers (DP20) with high dispersity synthesized d) in water e) 80:20 ACN: water and f) 80:20 DMF: water. All polymers correspond to DMA capped with CTA ($C_7H_7N_2S_2$)($CH_2CHCON(CH_3)_2)_{12}$($C_4H_7O_2$)).

organic solvents).

2.2. Effect of targeting various degrees of polymerization

We were subsequently interested to study how the degree of polymerization (DP) would affect the Đ control. In a series of experiments, we targeted polymers with a DP of 50, 100, 200 and 400.

The first reactions were conducted in organic/aqueous mixtures with an increased organic content ([DMF]:[H_2O] = 4:1) and the results are summarized in Fig. 3. For DP = 50 and DP = 100 (Fig. 3a-b, Table S5-6), Đ ranges of 1.15–1.56 and 1.19–1.68 were obtained, respectively, when all polymerizations had reached very high monomer conversions. As can be concluded from the previous section, when targeting DP = 200, the minimum Đ achieved was 1.31 (Đ range is 1.31–1.76, Fig. 3c, Table S4). However, for DP = 400 no satisfactorily control over Đ was possible. In particular, even when 12 equivalents of acid were employed, the Đ could not drop below 1.58, thus highlighting the limitations of the system to control Đ at higher DPs (Fig. 3d, Table S7). This was attributed to the nature of the solvent which does not allow for the sufficient protonation of the RAFT agent.[59,60] To bypass this, we sought to increase the monomer concentration from 20% v/v to 50% v/v and indeed by minimizing the solvent content, a lower Đ could be achieved when identical acid equivalents were employed (when using 6 equivalents of acid the lowest Đ at 20% v/v was 1.31 and the value was further decreased to 1.23 at 50% v/v monomer concentration, Figure S3a&c, Table S4&S8). To fully circumvent this issue, we replicated the experiments in aqueous media (at 20% v/v). Pleasingly, excellent Đ control could be achieved not only for DP = 50 and DP = 100 but also for DP = 200, DP = 400 and DP = 800 (Figure S4, Tables S1&S10-13). More specifically, the higher the DP, the wider the Đ range that could be obtained while more equivalents of acid were required to achieve the lowest possible Đ. In addition, when the RAFT agent was unprotonated, [55,58,61] a higher Đ could be obtained for higher DPs. For instance, for DP = 50 the Đ range was relatively narrow (1.14–1.49), and the lowest Đ was obtained when 1 equivalent of sulphuric acid was utilized while the unprotonated RAFT agent led to a Đ of 1.49. Instead, for DP = 800, a broader Đ range was achieved (1.22–1.67), the lowest Đ was attained at much higher acid concentrations (i.e. > 6 equivalents) and in the absence of acid a much higher Đ was displayed (i.e. 1.67). It is therefore apparent that much better control over Đ can be achieved in pure aqueous media for various targeted DPs. It is also noted that in contrast to DMF, when higher monomer concentrations were employed in water, (e.g. 50% v/v instead of 20% v/v) slightly higher Đs were obtained (Figure S3b&d, Table S9).

2.3. Effect of various organic solvents

Given the limitation of DMF to satisfactorily lower polymer Đ, a range of alternative solvents were also explored. First, high Đ PDMA was prepared (DP20) in a range of different solvents -such as H_2O, DMF, dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), acetonitrile (ACN) and dioxane- and matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-ToF-MS) was performed to investigate the chain end-group fidelity of the syntheses (Fig. 4d-f&S5d-f). Pleasingly, in all cases, a single polymeric species was evidenced, corresponding to CTA functionalized PDMA, albeit with Li^+, Na^+ and K^+ adducts. This indicates that high end-group fidelity could be achieved for all solvents, even when high dispersity values were targeted. We also highlight that in these syntheses very low concentrations of free radical initiator were utilized (<0.03 equivalents w.r.t RAFT agent), so these peaks were not visible in the MALDI-ToF-MS.

We therefore selected these solvents, in turn, so to investigate the effect of adding acid on the dispersity range obtainable in each medium (Tables S14-19, Figure S5). In a similar fashion to DMF, DMAc failed to yield very low Đ values, as even at 24 equivalents of acid the minimum Đ achieved was 1.36 (Figure S5b, Table S14). It is also noted that when these two solvents were employed, in combination with high acid concentrations (>2 equivalents), a side reaction could be detected *via* ^{1}H NMR whereby sulphuric acid reacted with the solvent thus leading to solvent degradation (Figure S6-8). This side reaction and the chain transfer to solvent constant of DMF could also be, partially, responsible for the higher dispersities obtained.[62] However, it is worth

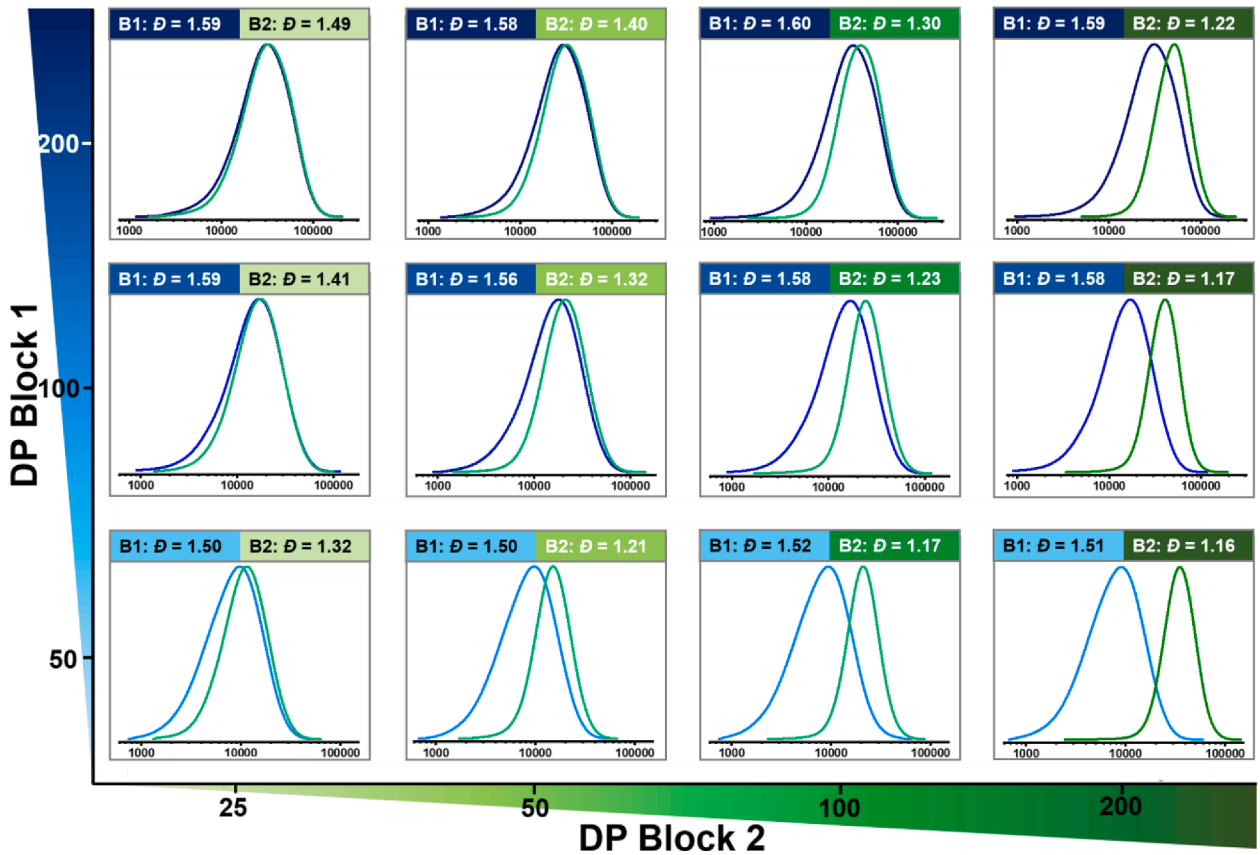

Fig. 5. The effect of the DP of the second block on the overall dispersity of diblock copolymers prepared by RAFT polymerization. In all cases the reactions were performed in pure water, with the CTA unprotonated for the first block and fully protonated for the second block. The DP of the first block was varied between 50 and 200 and the DP of the second block was varied between 25 and 200. In all plots, the x-axis represents the molecular weight and the y-axis represents normalized dw/dlogM as obtained by SEC.

mentioning that despite the side reaction, very high livingness could be maintained in both solvents as evident by successful *in-situ* chain extension experiments (Figure S10, Table S19).

Dimethyl sulfoxide (DMSO) was then selected as a solvent (Figure S5c, Table S15). Although no side reaction was found in this solvent, the lowest *Đ* achieved was 1.23 when 20 equivalents of sulphuric acid were employed. Nevertheless, a broad *Đ* range could be targeted (1.23–1.79) thus revealing the potential of this solvent, especially considering that DMSO is a medium in which both hydrophilic and relatively hydrophobic monomers are soluble.[63,64] Dioxane also proved to be a suitable solvent for *Đ* control resulting in a broad *Đ* range (1.17–1.86) while the lowest possible *Đ* was attained in the presence of 4 equivalents of acid (Figure S5a, Table S16). Perhaps the most promising organic medium was ACN (Fig. 4b, Table S17) as in the presence of just 2 equivalents of acid a *Đ* of 1.19 could be obtained. The total range achieved was also relatively broad (1.19–1.66) therefore establishing ACN as an excellent alternative to aqueous media. For a more meaningful comparison with the other solvents, when 2 equivalents of acid were used very high *Đ*s were achieved for DMAc and DMF (1.66 and 1.55 respectively), while DMSO and dioxane led to much lower *Đ*s (1.37 and 1.29 respectively). As such, it can be concluded that both ACN and water are very successful in controlling the *Đ* of homopolymers at low acid concentrations. Free radical polymerizations were also performed in these solvents and the result shows the maximum achievable molar mass obtained exceeded 200 kDa in all cases, which is higher than that of high-dispersity polymers made in the presence of unprotonated RAFT agent, confirming the polymerization is controlled under RAFT mechanism (Figure S11 and Table S20). Indeed, it should be highlighted that in pure ACN (rather than in 80:20 ACN: H_2O) just 0.5 equivalents of acid were required to obtain a final polymer with a dispersity as low as 1.25, further exemplifying ACN as an effective alternative to water (Figure S9, Table S18). These results show that in order to achieve similar dispersities, various amounts of acid were required to achieve the same protonation degree of the RAFT agent in different solvents (Fig. 4a-c, Figure S5a-c, Table S1, S4, S14-S17). To correlate the protonation state of the switchable RAFT agent in different media (e.g., deuterated DMSO and D_2O), the chemical shift of pyrinidyl ring hydrogen of the RAFT agent was characterized by ^{1}H NMR spectra (Figure S12).[56] It is shown that in deuterated DMSO higher equivalents of acid was needed to protonate the RAFT agent than in D_2O. Despite the high amounts of acid added, the RAFT agent is stable in organic solvent (DMSO-d_6) while a small amount (0.8%) of the ester bonds of the RAFT agent R group was hydrolyzed (Figure S13-S15). Importantly, the Z-group of the RAFT agent was not influenced by the acid and therefore the polymer livingness was not affected (Figure S17 & Table S24).

2.4. Synthesis of Đ–controlled diblock and triblock copolymers with varying degrees of polymerization

After establishing optimal conditions to control *Đ* in homopolymers, we were interested in assessing how the DP of the added second block would affect the final *Đ* of the diblock. To study this, we first synthesized three homopolymers at various DPs using the deprotonated RAFT agent (i.e. DP 50, DP = 100, DP = 200). We then varied the amount of monomer added for the second block (aiming for the second block to be composed of either DP = 25, or DP = 50, or DP = 100 or DP = 200) while utilizing an excess of acid which would enable the sufficient switch to a fully protonated macroCTA (Fig. 5, Table S21). In particular, when starting from a relatively low DP for the first block (DP = 50, initial *Đ* ~1.50), the *in-situ* addition of DP = 25 or DP = 50 already led to a

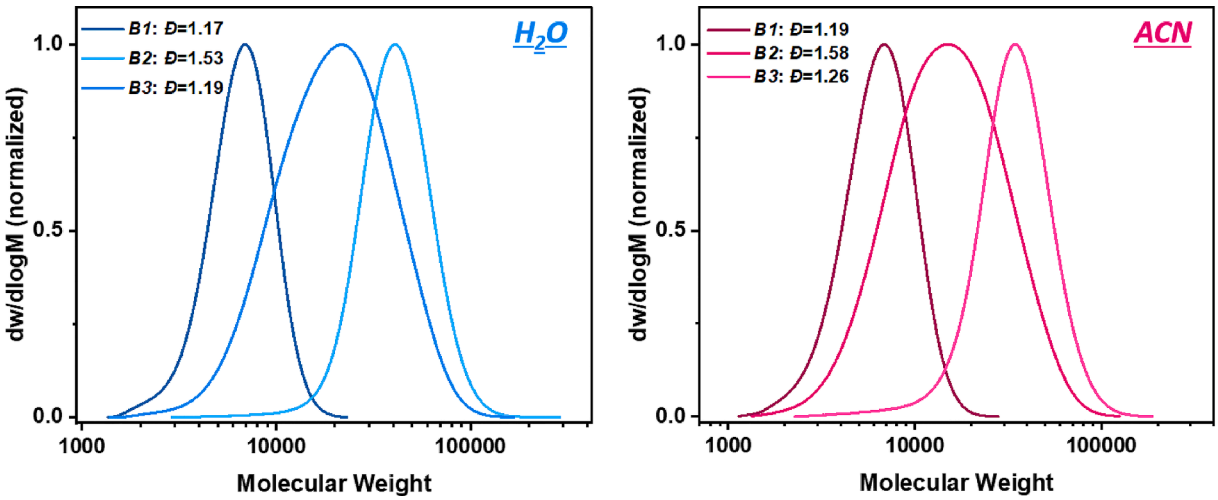

Fig. 6. SEC data for triblock copolymers prepared in a) aqueous and b) organic media. In both cases, the reactions were performed with the CTA protonated for the first and third blocks and unprotonated for the second block.

significant decrease in the overall Đ of the diblock resulting in a final Đ of 1.32 and 1.21, respectively. By further increasing the DP of the second block to DP = 100 and DP = 200 even clearer shifts were observed by SEC and the Đ of the diblock was reduced to 1.17 and 1.16, respectively. Therefore, it can be concluded that a macroCTA of DP = 50 can be satisfactorily chain-extended to yield diblocks with narrow molar mass distributions upon the addition of a minimum DP of 50. A slightly different profile was observed when a macroCTA of DP = 100 (Đ=1.58) was employed. On this occasion, neither the addition of DP = 25 nor DP = 50 could dramatically reduce the Đ (Đ=1.41 and Đ =1.32, respectively). However, when the DP of the second block was increased to DP = 100 and DP = 200, narrow molar mass distributions could be obtained yielding diblocks with a Đ of 1.23 and 1.17 respectively. Upon replicating the experiments utilizing a DP = 200 macroCTA (Đ=1.59), we found that a diblock with Đ ~1.22 was only possible when 200 equivalents of monomers were added. Instead, upon targeting DP = 25, DP = 50 and DP = 100 for the second block, only higher overall Đ diblock copolymers could be prepared (Đ=1.49, Đ=1.40 and Đ=1.30). From these experiments we can conclude the following:

(i) The targeted DP of the second block can significantly affect the final Đ in diblock copolymers.
(ii) The higher the DP of the added block, the lower the Đ of the diblock.
(iii) The higher the DP of the starting macroCTA, the more monomer is required to be added to bring the overall Đ of the diblock down to ~ 1.2. This suggests that the efficient protonation of the macroCTA alone is not sufficient to control polymer Đ and that the length of the added block should also be considered.
(iv) To target diblock copolymers with a wide range of Đ (i.e. a large difference between the dispersity of the homopolymers and the diblock copolymer), the length of the added block should be equal or higher to the length of the macroCTA (i.e. $DP_{added\ block} \geq DP_{macroCTA}$). To verify this was also the case for DP = 200, we did a control experiment whereby 300 equivalents of monomer were added during the *in-situ* chain extension and the overall Đ of the diblock could be further decreased to 1.19 (Figure S16, Table S22).

Last, but not least, we applied the acquired knowledge in designing two triblock copolymers with alternating low and high Đ in both aqueous and organic media (ACN). Specifically, by using the fully protonated RAFT agent, a homopolymer with a Đ of 1.17 (DP = 50) was first obtained. Upon adding 75 equivalents of the next monomer and in the presence of a base, we were able to increase the overall Đ of the diblock to 1.53 (Fig. 6, Figure S17, Table S23). Once the diblock reached quantitative monomer conversion, we added the next monomer together with acid and brought the Đ of the triblock down to 1.19. Pleasingly, very similar data could be attained in both solvent systems leading to well-defined triblock copolymers with remarkable control over their Đ (Fig. 6, Figure S17, Table S24).

3. Conclusion

In summary, we found that the nature of the organic solvent can significantly affect the Đ control in homopolymers. While DMF and DMAc could not generate very low Đs, in particular when higher DPs were targeted, alternative solvents were examined including water, dioxane, ACN and DMSO. Water and ACN were proven to be the ideal solvents to control polymer Đ regardless of the targeted DP. Importantly, very high livingness could be obtained regardless of the starting Đ. The effect of the targeted DP proved to also be an important parameter to consider during the synthesis of both homopolymers and diblock copolymers. For homopolymers, the lower the DP the less acid was required to minimize the Đ (down to ~ 1.2) while in diblock copolymers we found that the DP of the added block must be equal or higher to the DP of the macroCTA in order to ensure that low Đ is feasible. Exemplary triblock copolymers in both organic and aqueous media were also synthesized with alternating low and high Đs showing the versatility of our methodology.

CRediT authorship contribution statement

Maria-Nefeli Antonopoulou: Investigation, Writing – original draft, Visualization. **Richard Whitfield:** Investigation, Writing – review & editing. **Nghia P. Truong:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Athina Anastasaki:** Conceptualization, Writing – original draft, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

All relevant data are within the manuscript and available from the corresponding author upon request.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2022.111326.

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