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Synthesis of well-defined α,ω-telechelic multiblock copolymers in aqueous medium: *In situ* generation of α,ω-diols

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Abstract

The synthesis of well-defined α,ω-dihydroxyl telechelic multiblock copolymers by sequential *in situ* chain extensions *via* aqueous Cu(0) mediated living radical polymerization (SET-LRP) is reported. The rapid disproportionation of Cu(I)Br in the presence of Me_6-TREN in water has been exploited to generate Cu(0) and [$Cu(II)Br_2$/Me_6-TREN] *in situ*, resulting in rapid reaction rate and narrow molecular weight distributions. Under optimized conditions, a telechelic heptablock copolymer was obtained within 2 hours with a final dispersity of ~ 1.1 while the monomer conversion was > 99% for each block. A range of acrylamides and acrylates have been successfully incorporated within the same polymer backbone, including *N*-isopropylacrylamide (NIPAAm), *N,N*-diethylacrylamide (DEA) and *N,N*-dimethylacrylamide (DMA) and poly(ethylene glycol) methyl ether acrylate ($PEGA_{480}$). The thermo-responsive nature of these materials was subsequently demonstrated *via* cloud point measurements as both a function of molecular weight and backbone functionality. In addition, the typically unwanted hydrolysis of the α- and ω- end groups in aqueous media was further exploited via isocyanate post-polymerization modifications to alter the end group functionality.

Introduction

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The synthesis of acrylamide, acrylate or methacrylate based macromolecules has been widely reported using Nitroxide-Mediated Polymerization (NMP),[1] Reversible-Addition Fragmentation chain Transfer polymerization (RAFT)[2] or Transition-Metal Mediated Reversible-Deactivation Radical Polymerization (TMM-RDRP)[3, 4] in organic solvents. However, the introduction of water in the solvent composition has proved to be challenging, as the control over the molecular weight distributions is often difficult to retain, especially in copper mediated-RDRP polymerizations, due to an increase in termination events.[5, 6] Undesired side reactions, such as reversible dissociation and substitution of the halide ligand from the Cu(II) complex can occur, resulting in inefficient deactivation of a growing polymer chain and loss of control.[7] Moreover, additional side reactions are commonly reported in water, such as loss of end group fidelity *via* hydrolysis.[8] Numerous optimizations in both aqueous solutions and organic solvents have been conducted to diminish side reactions and retain narrow molecular weight distributions and high end group(s) fidelity, mainly by *in situ* regeneration of the transition metal catalyst by various stimuli.[9] Several ATRP techniques[10-29] have proved to be powerful tools, yielding functional macromolecular structures in various solvents. Nevertheless, the synthesis of bio-compatible monomers such as *N*-isopropylacrylamide (NIPAAm) and/or other acrylamides has remained a challenge in water.[8, 30-32] Indeed, the use of highly polar organic solvents (alcohols and DMF preferentially) or binary mixtures with water are necessary to achieve good control over the molecular weight distributions under standard ATRP conditions.

The controlled incorporation of different hydrophilic and/or thermo-responsive monomers into the same polymer backbone, such as poly(ethylene glycol) methyl ether acrylate ($PEGA_{480}$), NIPAAm, *N,N*-dimethylacrylamide (DMA) and *N,N*-diethylacrylamide (DEA) is highly desirable and has not yet been realized. The facile tuning of the copolymer properties (*e.g.* LCST), providing access to the rapid synthesis of "smart-materials" has attracted significant interest, especially in biomedical applications,[33] from tissue engineering to biosensing. Thus, studies have been conducted in to the design of macromolecular architectures[34, 35] through side chain functionalities and end group modifications, in order to manipulate the LCST, as small changes can be detrimental towards the biocompatibility of the material.[36] Perrier and co-workers have recently reported the synthesis of multiblock copolymers in both aqueous and organic media utilizing an optimized RAFT approach.[37, 38] Although different degrees of polymerization have been achieved (DP_n=3-100 per block), the high reaction temperature (70°C) is not suitable for the polymerization of thermo-responsive monomers (*e.g.* NIPAAm, DEA) that possess an LSCT below 70°C in aqueous solution. In addition, the RAFT is limited to acrylamides as polymerization of other monomers (*e.g.* acrylates) at these temperatures results in unwanted side reactions and unavoidable termination.[39, 40] Copper-mediated RDRP approaches have attempted to address these issues, although only organic solvent systems were successfully employed.[41-43] There is only one example in literature reporting the synthesis of

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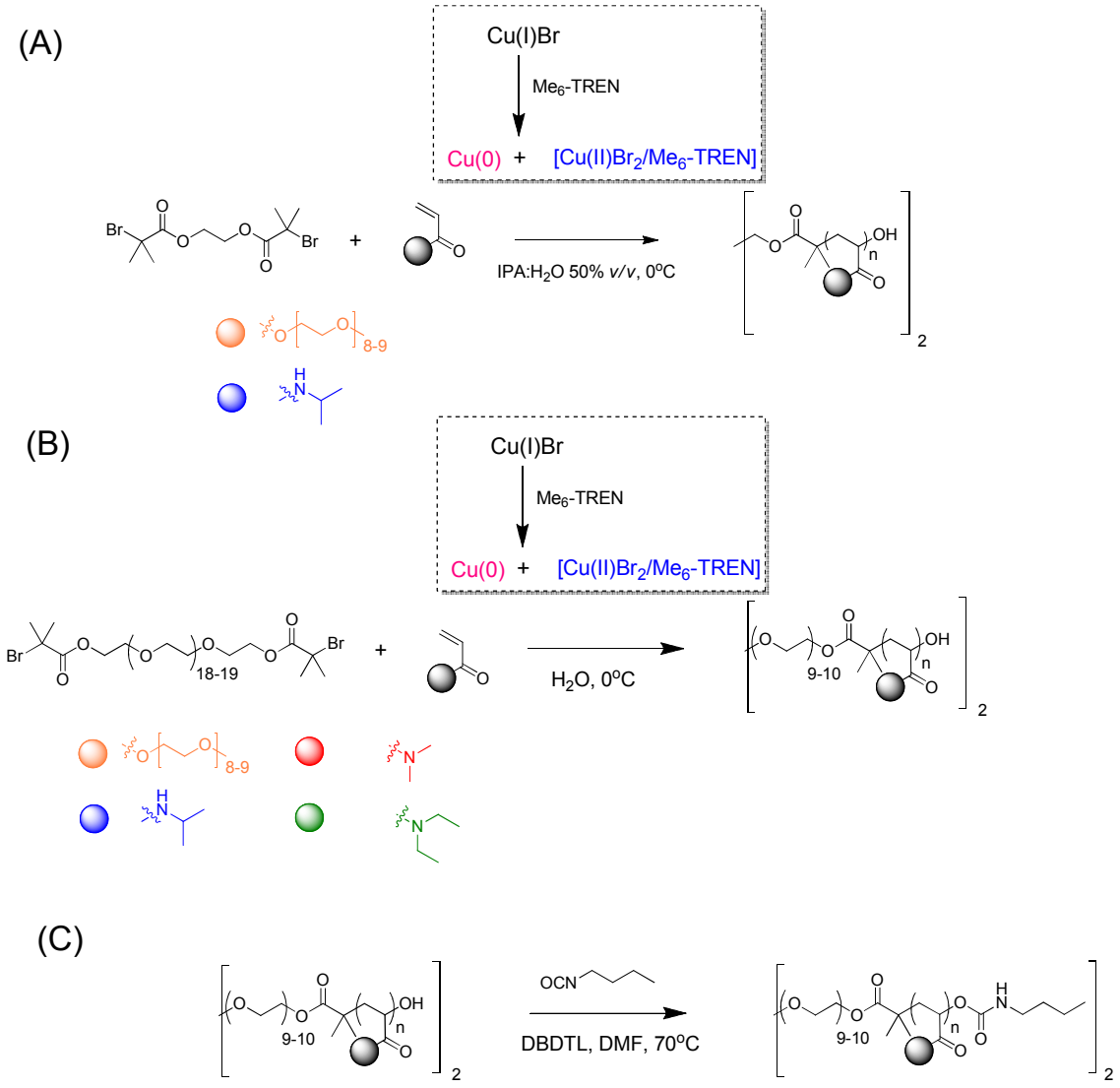
multiblocks at ambient temperature or below in water and in this study only acrylamides were reported avoiding issues arising from different reactivity ratios (*e.g.* acrylamides and acrylates).[44]

Recently, Haddleton *et al.*[26, 45] exploited the rapid and quantitative disproportionation of Cu(I)Br in the presence of the *N*-donor aliphatic ligand, *N,N,N',N',N'',N''*-hexamethyl-[tris(aminoethyl)amine] (Me_6-TREN), in water[26, 46] and complex aqueous mixtures[47, 48] prior to polymerization to yield poly(acrylates) and poly(acrylamides) with an excellent degree of control. Thus, utilizing this robust technique for the synthesis of more sophisticated architectures including stimuli-responsive hydrogels,[49] double-hydrophilic (co)polymers[50] and organized nanostructures[51] (such as micelles,[52] flower-like micelles,[53-55] vesicles, polymersomes) would be highly desirable. Such architectures can be obtained using functional initiators and post-polymerization modifications[56]. Towards this, the use of bi-functional entities could maximize the time limit arising from chain-end hydrolysis[8, 44] in aqueous medium as more functionality can be introduced upon each monomer addition.[57] Nevertheless, the employment of such initiators is rather challenging in water, considering the high rate of termination due to the increase in number of generated radicals.

Herein, the versatility of aqueous SET-LRP was exploited for the polymerization of hydrophilic and/or thermo-responsive monomers including $PEGA_{480}$, NIPAAm, DEA and DMA in both aqueous and mixtures of organic/aqueous media (Scheme 1). Two different types of bi-functional initiators have been employed to yield well-defined multiblock copolymers with narrow dispersity values ($Đ$ < 1.19) and quantitative conversions (> 99 % by ^{1}H NMR) by sequential monomer addition. Remarkably, both acrylates and acrylamides could be combined within the same polymer backbone, yielding a heptablock copolymer with narrow dispersity (> 99 % conversions, $Đ$ < 1.11) in two hours. The LCST response of the copolymers[58-61] was further investigated as function of molecular weight, monomeric composition and chain-ends functionality. Moreover, the unavoidable hydrolysis of the halogen end groups has been exploited to incorporate additional functionalities *via* isocyanate coupling post-polymerization.



Scheme 1. Synthetic route to yield *α,ω*-dihydroxyl telechelic polymers in aqueous medium. (A) Aqueous SET-LRP using bi-functional initiator in IPA:H_2O 50% *v/v*. (B) Aqueous SET-LRP using PEG based bi-functional initiator in H_2O. (C) Hydrophobic modification of diols using butyl isocyanate in DMF.

Results and discussions

The polymerization of $PEGA_{480}$ in water was attempted using the bi-functional initiator, ethylene bis(2-bromoisobutyrate) (Figures S1-S3). However, the solubility of the initiator in water proved to be limited and was rectified by the addition of a co-solvent, (up to a 50 % *v/v* ratio). 2-Isopropanol (IPA) became the co-solvent of choice due to low toxicity and high polarity, which was thought would

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minimize disruption of the disproportionation equilibrium of Cu(I)Br/Me_6-TREN. In order to test this, UV Vis experiments were conducted, revealing quantitative disproportionation of Cu(I)Br when a binary mixture of IPA and water (50 % *v/v*) was employed (Figures S8-S9). Cu(I)Br was allowed to disproportionate in water (15 min) prior to polymerization to ensure the rapid and quantitative formation of Cu(0) and [Cu(II)Br_2/Me_6-TREN]. Upon addition of monomer ($PEGA_{480}$, DP_n=20), initiator and solvent (IPA/water), near quantitative monomer conversion (> 99%) and narrow molecular weight distributions (M_n = 5500 g.mol^{-1}, $Đ$ =1.11) were observed within 2 hours, as evidenced by both ^{1}H NMR and SEC (Figure 1 and S10). It is important to note that in comparison with mono-functional initiators, higher amounts of Cu(I)Br (which subsequently disproportionates yielding more deactivator Cu(II)Br_2) are required in order to achieve good control over the molecular weight distribution due to the increase (2 fold) in the number of initiation sites. The [I]:[M]:[Me_6-TREN]:[Cu(I)Br] was adjusted from 1:20:0.4:0.4 (typically employed for monofunctional initiators) to 1:20:0.4:0.8. The amount of ligand was maintained as an excess of ligand has been previously reported to compromise the end group fidelity due to termination events and side reactions[6, 7, 62].

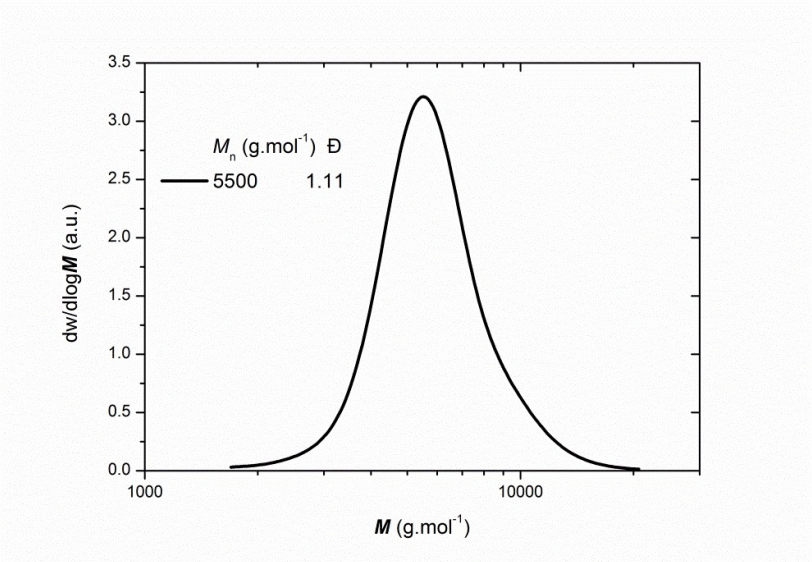

Figure 1. SEC trace ($CHCl_3$ eluent) of poly[poly(ethylene glycol) methyl ether acrylate] (99 % conv. by ^{1}H NMR), [I]:[M]:[Me_6-TREN]:[Cu(I)Br] 1:8:0.4:0.8 initiated by ethylene bis(2-bromoisobutyrate).

The polymerization of $PEGA_{480}$ was significantly slower than previously reported in pure water,[26] suggesting that IPA was responsible to a relative retardation in the rate of polymerization. Similar results with respect to rate of polymerization (2 hours) were obtained when low molecular weight PNIPAAm were targeted, though high monomer conversions (92 % by ^{1}H NMR) and narrow dispersities ($Đ$ = 1.11) were achieved (Figures S11-S12). Interestingly, when higher molecular weights of PNIPAAm (M_n > 4000 g.mol^{-1}) were targeted, the use of co-solvents had a detrimental

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effect, resulting in cessation of polymerization. The insolubility of PNIPAAm in the selected alcoholic mixtures[48, 63, 64] results in phase separation of the polymer from the catalytic system. Investigations were subsequently conducted to lower the amount of alcoholic co-solvent. Unfortunately, the initiator was not fully soluble in mixtures of IPA and water lower than 50 % *v/v* which compromised the monomer conversion (< 90 %) for degrees of polymerization greater than 30 (M_n > 4000 g.mol^{-1}). Moreover, at the end of the polymerization, the reaction mixture was green suggesting the formation of Cu(II) species, while no visible Cu(0) was observed. This implies a large extend of termination events[22] and compromises the control over the polymerization in that particular solvent composition.

Consequently, a second bi-functional water soluble initiator derived from linear poly(ethylene glycol) (PEG, av. M_w = 1000 g.mol^{-1}) was synthesized and characterised by NMR and MALDI-ToF MS (Figures S4-S7), to overcome both solubility and precipitation issues. Similar linear PEG ATRP/SET-LRP initiators have been widely studied for the synthesis of responsive block copolymers that self-assemble in micelles, vesicles and rods.[52] However, the synthesis of such functional macromolecular structures has been challenging by Cu-mediated processes in aqueous systems[65] due to enhanced termination events as discussed previously.[6]

Thus, the obtained telechelic PEG initiator was employed for the aqueous polymerization of NIPAAm. Unexpectedly, when a ratio [I]:[Me_6-TREN]:[Cu(I)Br] 1:0.4:0.8 was employed, relatively limited conversions were observed after 30 minutes (80 % by ^{1}H NMR, Figure S16). To enhance the polymerization rate, the [Cu(I)Br]/[ligand] ratio was adjusted by slightly increasing the ligand concentration. The optimized ratio of [I]:[Me_6-TREN]:[Cu(I)Br] = 1:0.6:0.8 resulted in a pronounced increase of the polymerization rate (> 99 % by ^{1}H NMR in 30 minutes) while narrow dispersities were retained ($Đ$ < 1.15) (Figures S17-S18). Moreover, when higher degrees of polymerization were targeted (DP_n = 160-320), higher concentrations of both ligand and copper were needed to retain control, in agreement with previously reported experiments.[26, 45] When higher concentrations of just ligand were employed, poor control over the molecular weight distributions was observed (Figures S19-S20). It is therefore evident that careful optimization of ligand to copper concentration is required to achieve good control while maintaining a rapid polymerization rate, as small changes can have unsatisfactory effects on the polymerization. Pleasingly, near quantitative monomer conversions (> 99 % by ^{1}H NMR) were attained within 30 minutes for various degrees of polymerization of NIPAAm (DP_n = 20-320) with SEC showing symmetrical narrow molecular weight distributions in all cases ($Đ$ < 1.19, Figure 2).

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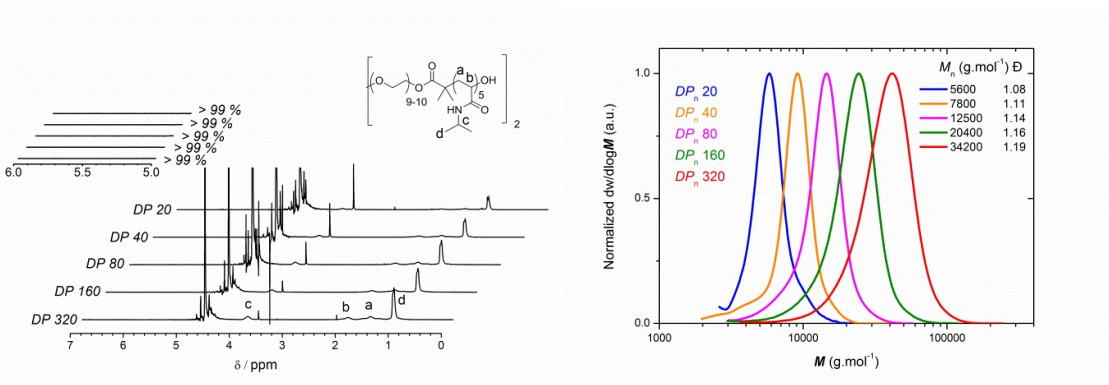

Figure 2. Monitoring the polymerization of *N*-isopropylacrylamide in H_2O at 0°C after 30 minutes by ^{1}H NMR (D_2O, 250 MHz). SEC traces (DMF eluent) of poly(*N*-isopropylacrylamide) (> 99 % conv. by ^{1}H NMR) with different degrees of polymerization, initiated by poly(ethylene glycol) bis(2-bromoisobutyrate).

In order to probe the end group fidelity of the obtained telechelic poly(NIPAAm), a second aliquot of NIPAAm was added *in situ* at high conversion (first NIPAAm block, DP_n = 80, > 99 % conversion by ^{1}H NMR after 30 minutes, M_n 13800 g.mol^{-1}, $Đ$ = 1.17) without the need for purification steps prior to addition. Excellent control was observed (> 99 % conversion by ^{1}H NMR, M_n = 24700 g.mol^{-1}, $Đ$ = 1.17) with the molecular weight distribution shifting to higher molecular weight without any visible tailing at high or low molecular weights (Figures S21-S22), suggesting high retention of the α,ω-bromine end groups throughout the polymerization. Similar results were obtained when $PEGA_{480}$ was employed as monomer, at various degrees of polymerization (Figures S25-S26). High monomer conversions (> 95 % by ^{1}H NMR) were attained in 30 minutes with excellent control, as illustrated by narrow molecular weight distributions ($Đ$ < 1.15). However, in the latter case, a minor tailing at high molecular weights was observed which is most likely attributed to the presence of diacrylate impurities in the monomer, consistent with previous reports in the literature.[66, 67]

Since end group fidelity appeared to be high throughout polymerization, and assuming that chain extension should occur in a reasonable timescale prior to hydrolysis[44], we were intrigued to test the potential towards multiple side chain functionalities *via* sequential addition processes. Secondary (NIPAAm), and tertiary (DMA, DEA) acrylamides as well as acrylates ($PEGA_{480}$) show stimuli-responsive behaviour and are popular due to the availability, ease of handling and breadth of understanding in functional macromolecular design. Thus, combination of the properties of those monomers *via* rapid and quantitative polymerization in aqueous media would be advantageous. Firstly, the synthesis of acrylamide-based block copolymers was tested using the bi-functional PEG initiator. The high α,ω-bromide end group fidelity of the telechelic PNIPAAm structure enables the synthesis of well-defined $PDEA_{4\text{-}5}$-*b*-$PNIPAAm_5$-*b*-PEG-*b*-$PNIPAAm_5$-*b*-$PDEA_{4\text{-}5}$ with near

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quantitative monomer conversion (> 99 %) and low dispersities ($Đ$ < 1.13, Figure 3). Telechelic PNIPAAm was also chain extended with DMA in order to modify the properties of the final (co)polymer (Figures S23-S24), yielding well-defined pentablock copolymers in a total reaction time of one hour.

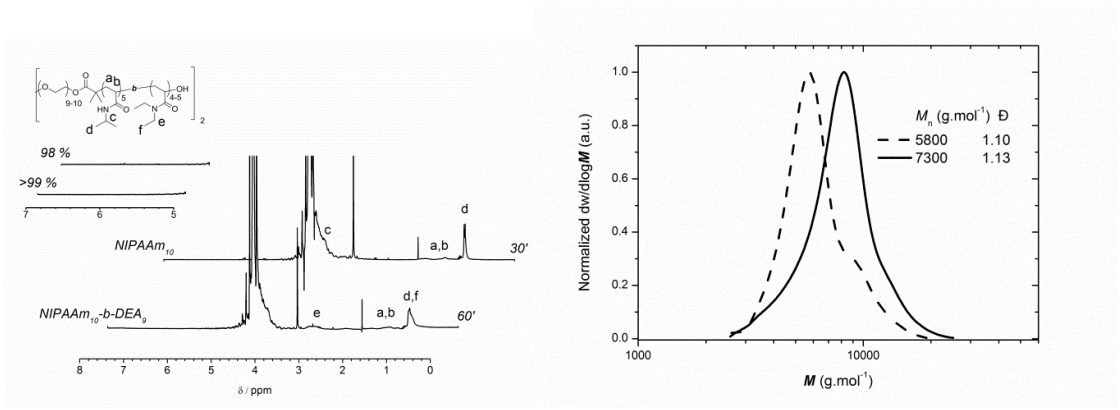

Figure 3. Monitoring of the chain extension of poly(*N*-isopropylacrylamide) in H_2O at 0°C with *N,N*-diethylacrylamide by ^{1}H NMR (D_2O, 250 MHz). SEC traces (DMF eluent) of chain extension of poly(*N*-isopropylacrylamide)$_{10}$ (98% conv. by ^{1}H NMR, M_n 5800 g.mol^{-1}, $Đ$ = 1.10) initiated by poly(ethylene glycol) bis(2-bromoisobutyrate) with *N,N*-diethylacrylamide (101 µL, 9 eq.).

Encouraged by these initial results, we were intrigued to test the versatility by combining acrylate and acrylamides (secondary and tertiary). Although, the incorporation of monomers that exhibit different activities (*e.g.* acrylates and acrylamides) is rather challenging, a well-defined telechelic heptablock copolymer DMA$_{10}$-*b*-NIPAAm$_{10}$-*b*-PEGA$_{480,10}$-*b*-PEG-*b*-PEGA$_{480,10}$-*b*-NIPAAm$_{10}$-*b*-DMA$_{10}$ was obtained within two hours of reaction time. To the best of our knowledge, this is the first time that such a complex composition has been achieved within such a short time frame.

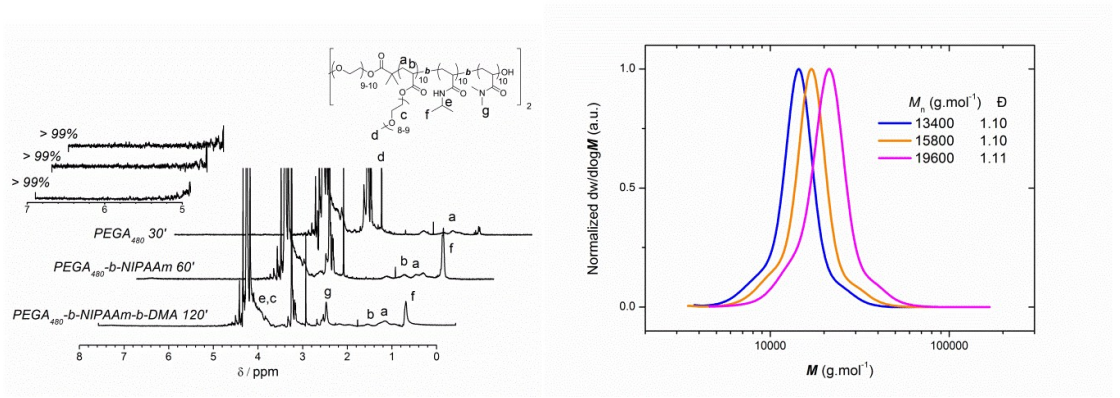

Figure 4. Monitoring the chain extension of poly[poly(ethylene glycol) methyl ether acrylate] in H_2O at 0°C upon sequential addition of *N*-isopropylacrylamide and *N,N*-dimethylacrylamide by ^{1}H NMR

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(D_2O, 250 MHz). SEC traces (DMF eluent) of multiblock copolymer $PDMA_{10}$-*b*-$PNIPAAm_{10}$-*b*-$PPEGA_{480,10}$-*b*-PEG-*b*-$PPEGA_{480,10}$-*b*-$PNIPAAm_{10}$-*b*-$PDMA_{10}$.

More importantly, the DMA_{10}-*b*-$NIPAAm_{10}$-*b*-$PEGA_{480,10}$-*b*-PEG-*b*-$PEGA_{480,10}$-*b*-$NIPAAm_{10}$-*b*-DMA_{10} heptablock copolymer presented excellent control over the molecular weight distributions for the final material ($Đ$ < 1.11, Figure 4), while high monomer conversions were attained for each individual block (> 99 % by ^{1}H NMR), prior to addition of the next monomer. Residual shoulders can be observed on the SEC traces at high molecular weights (ascribed to the presence of diacrylates in the $PEGA_{480}$[66]). Tailing at low molecular weight can be attributed to the limited, yet visible, extend of contamination with mono-functional initiator traces considering the differences in M_p (8000 g.mol^{-1} and 14500 g.mol^{-1} for the first block). It should be noted that such high detail in our system is visible because of the narrow molecular weight distributions. However, the successful integration of three different monomeric moieties highlights the high robustness and versatility of the polymerization technique.

When the desired macromolecular composition is obtained and no additional monomer is injected, the halogen chain ends were left to hydrolyse[8, 68] (over at least 8 hours) in the aqueous solution, resulting in dihydroxyl functional *α,ω*-end groups. So far, the unavoidable termination *via* hydrolysis has usually been considered as a limitation of the polymerizations in aqueous media as the resulting macrodiol cannot re-initiate polymerization (typically a few hours).[44] However, during this investigation the substitution of the *α,ω*-Br by water to form nucleophilic *α,ω*-OH enables the introduction of additional functionalities *via* reaction with monoisocyanates to the polymer end groups.[67, 69] The post-polymerization modification was carried out in a dry organic solvent, avoiding the presence of air and residual water, utilizing butyl isocyanate as the selected end-capping moiety. After lyophilisation, the successful modification of the copolymer was examined by ^{1}H NMR. The presence of butyl *α,ω*-chain ends is highlighted by the appearance of peaks at 2.17, 1.48, 1.17 and 0.87 ppm (Figures S26-S28). Moreover, the comparison of the integration of the peaks at 2.17 ppm (HN-C***H***$_2$-CH_2-CH_2-CH_3) and 0.87 ppm (HN-CH_2-CH_2-CH_2-C***H***$_3$) reveals 94 % end group fidelity by ^{1}H NMR, which implies that 94 % of the chains were hydroxyl terminated prior to functionalization (assuming all chains were *α,ω*–OH terminated). The remaining polymer chains are potentially terminated *via* combination, as noticed in previously reported studies.[26]

The preparation of multiblock copolymers with well-defined molecular composition allows us to precisely tune the cloud point of PNIPAAm. Using the bi-functional PEG based initiator, macro-diols containing secondary and tertiary acrylamides and/or acrylates were prepared. The LCST of NIPAAm based compounds has been widely studied,[58, 70] and implemented into the design of thermo-responsive "smart" materials.[71] The copolymerization of the thermo-responsive NIPAAm (LCST ~ 32-35°C) with a hydrophilic 'spacer' should increase the cloud point temperature (T_{cp}) of the macrodiol,

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compared to PNIPAAm with a similar molecular weight (LCST ~ 41°C, Figure S32). In order to verify this, the influence of the molecular weight of poly(NIPAAm) on the T_{cp} was investigated.

The influence of the PNIPAAm$_n$-*b*-PEG-*b*-NIPAAm$_n$ (co)polymers ($10 < n < 160$) molecular weights on the LCST transition is shown in Figure S39. In order to have a more accurate understanding of the system, one has to take into account the influence of the sample concentration and the end group functionality which can further affect the LCST transition.[72-74] An increase in molecular weight of PNIPAAm block resulted in a decrease of T_{cp} (71.3 - 41.2 °C). Furthermore, a decrease of the polymer solution concentration in water showed a decrease in T_{cp} for all DP_ns investigated (Figures S33-S37). Those evolutions of the LCST transition are common for homo and hetero-telechelic PNIPAAms of similar molecular weights (Figures S32 and S38).[72]

Subsequently, the influence of the presence of co-monomers on T_{cp} was investigated. Considering the high tolerance of our system towards acrylates and acrylamides, the thermo-responsive and/or hydrophilic properties of each monomer were combined, as previously discussed, in the same polymer chain. Thus, the considerable difference in thermal properties of DEA (theoretical LCST ~ 33°C)[75] and DMA (no LCST between 0-100°C)[76, 77] should have opposite effects on the LCST transition when included in the overall copolymer composition.

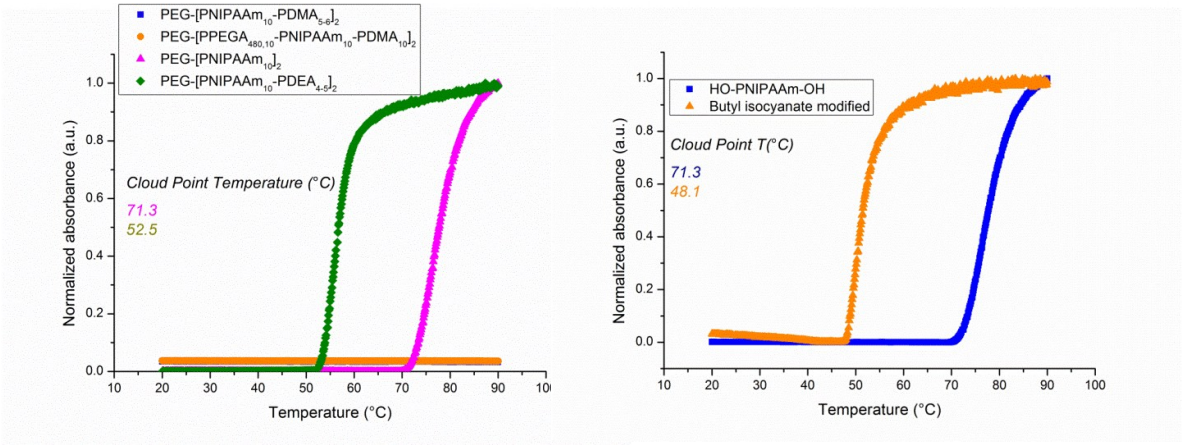

Figure 5. Modification of the cloud point temperature in H_2O of a poly(*N*-isopropylacrylamide)-*b*-poly(ethylene glycol)-*b*-poly(*N*-isoproylacrylamide) copolymer upon incorporation of additional backbone functionality (left) and of the hydrophobically modified poly(*N*-isopropylacrylamide)$_{10}$-*b*-poly(ethylene glycol)-*b*-poly(*N*-isopropylacrylamide)$_{10}$ in H_2O (right).

The turbidimetry curves highlight the effect of both co-monomers on the LCST transition temperature (Figure 5). The incorporation of DEA as a co-monomer is expected to result in a decrease of T_{cp}. Indeed, the overall cloud point of a PDEA$_{4-5}$-*b*-PNIPAAm$_{10}$-*b*-PEG-*b*-PNIPAAm$_{10}$-*b*-PDEA$_{4-5}$

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decreases from 71.3 °C (PNIPAAm$_{10}$-*b*-PEG-*b*-PNIPAAm$_{10}$) to 52.5 °C. Thus, it is shown that the composition of the copolymer can have a significant impact on T_{cp}. On the contrary, the incorporation of DMA onto the (co)polymeric backbone is expected to increase the overall LCST. However, within the limits of our instruments (5 °C < T < 90 °C), the temperature transition could not be observed, suggesting an increase of the LSCT beyond our upper temperature limit. Nevertheless, one could tune the stimuli-responsive properties of a copolymer by simple addition of a co-monomer, depending on the final application of the supramolecular structure.

Following successful addition of monoisocyanates to the *α*- and *ω*-chain ends of the (co)polymer effect on T_{cp} was investigated. The change in the hydrophobicity of the polymer end groups was expected to decrease the T_{cp} of the PNIPAAm$_{10}$-*b*-PEG-*b*-PNIPAAm$_{10}$ triblock copolymer. The T_{cp} of a hydroxyl-terminated PNIPAAm$_{10}$-*b*-PEG-*b*-PNIPAAm$_{10}$ was recorded at 71.3°C in water prior to modification. The modification of the chain ends with butyl isocyanate resulted in a decrease of T_{cp} to 48.1°C (Figure 5). This major decrease in T_{cp} (23.2°C) for the modified copolymer is more pronounced than previously reported for a non-telechelic PNIPAAm, modified *via* CuAAC post polymerization[78] (> 5°C) and is believed to be due to the telechelic nature of our materials and thus the introduction of two functionalities at the polymer chain ends. It should be noted that the presence of multiple hydrophobic chain ends favours the phase separation of the copolymer from the solvent, inducing a significant decrease of T_{cp}.[79, 80] Thus, the introduction of two hydrophobes instead of one induces a poorer miscibility of the copolymer in water, and a reduction of the copolymer mixing entropy *via* self-assembly (Figures S30-S31), which increases the local copolymer concentration.[81]

Conclusions

Herein we report the synthesis of *α,ω*-hydroxyl functionalized multiblock copolymers utilizing a diversity of hydrophilic and/or thermo-responsive monomers including PEGA$_{480}$, NIPAAm, DEA and DMA. The polymerizations were performed in aqueous and mixtures of aqueous/organic media employing two different types of bi-functional initiators. Upon careful optimization of the reaction conditions, narrow dispersed (*Đ* < 1.15) block copolymers were obtained in a near quantitative manner (>99% conversion by ^{1}H NMR upon each monomer addition). Noteworthy, the synthesis of a well-defined heptablock copolymer consisting of both acrylamides and acrylates could also be achieved within only two hours of overall reaction time without any need for purification between the iterative additions. More importantly, hydrolysis of the polymer end groups after polymerization was exploited to perform hydrophobic end group modification *via* isocyanate end-capping. Subsequently, the effect of the bi-functional initiator, multiblock composition and end group modification on the (co)polymer cloud point temperature was investigated in detail, paving the way for the rapid and facile synthesis of "smart" materials.

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Acknowledgments

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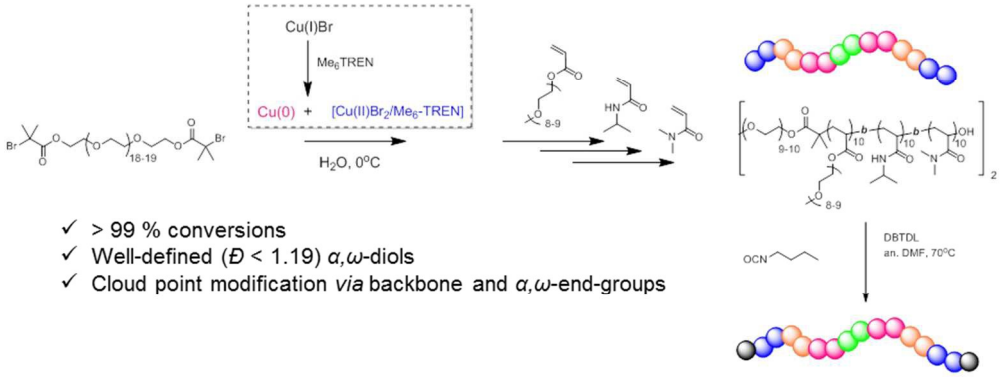

✓ > 99 % conversions
✓ Well-defined ($Đ$ < 1.19) α,ω-diols
✓ Cloud point modification *via* backbone and α,ω-end-groups

254x190mm (96 x 96 DPI)