Universal Conditions for the Controlled Polymerization of Acrylates, Methacrylates and Styrene via Cu(0)-RDRP

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ABSTRACT: Usually atom transfer radical polymerization (ATRP) requires various parameters, such as the type of initiator, transition metal, ligand, solvent, temperature, deactivator, added salts and reducing agents, need to be optimised in order to achieve a high degree of control over molecular weight and dispersity. These components play a major role when switching monomers e.g. from acrylic to methacrylic and/or styrenic monomers during the synthesis of homo- and block copolymers as the stability and reactivity of the carbon centered propagating radical dramatically changes. This is a challenge for both "experts" and non-experts as choosing the appropriate conditions for successful polymerization can be time consuming and an arduous task. In this work we describe some universal conditions for the efficacious polymerization of acrylates, methacrylates and styrene (using an identical initiator, ligand, copper salt and solvent) based on commercially available reagents (PMDETA, IPA, Cu(0) wire). The versatility of these conditions is demonstrated by the near quantitative polymerization of these monomer families to yield well-defined materials over a range of molecular weights with low dispersities (~1.1-1.2). The control and high end group fidelity is further exemplified by *in situ* block copolymerization upon sequential monomer addition for the case of methacrylates and styrene furnishing higher molecular weight copolymers with minimal termination. The facile nature of these conditions, combined with readily available reagents will greatly expand the access and availability of tailored polymeric materials to all researchers.

INTRODUCTION

The advent of reversible deactivation radical polymerization techniques (RDRP) has opened new avenues for the synthesis of advanced materials that exhibit narrow molecular weight distributions (MWDs), high end group fidelity and precisely controlled molecular weight and architecture. Amongst various polymerization approaches (e.g. reversible addition-fragmentation chain-transfer (RAFT)[1, 2], nitroxide mediated polymerization (NMP)[3] etc.), atom transfer radical polymerization (ATRP)[4, 5] and Cu(0)-RDRP[6-8] (typically referred to as either single electron transfer (SET)-LRP or supplemental activation and reducing agents (SARA)-ATRP) have significantly contributed to this field.

Both ATRP and Cu(0)-RDRP are considered as multicomponent systems typically composed of a metal source (Cu(I) or Cu(0)), a monomer (e.g. acrylates, methacrylates, styrene etc.), an initiator, a ligand, a solvent, a deactivator (e.g. $CuBr_2$, $CuCl_2$ etc.) as well as various other additives (e.g. salts, reducing agents etc.). To select the appropriate initiator, good knowledge of the reactivity of different alkyl halides towards initiation is important in order to maintain good control over the polymerization process and the polymer end groups, the latter example being especially important for the efficient synthesis of block copolymers.[1, 9-11] The selection of a suitable catalyst is also of importance as different reactivities could lead to vastly different rates of polymerization (k_p), thus compromising overall control of the polymerization.[1, 12] In addition the activity as well as the concentration of ligand plays an important role in the success of a polymerization with ligands ranging from very high (e.g. tris(2-pyridylmethyl)amine (TPMA), tris[2-(dimethylamino)ethyl]amine (Me_6Tren)) to very low activity (bipyridine (bpy), tetramethylethylenediamine (TMEDA)), where high activity corresponds to the ligand activity to stabilize Cu(II) relative to Cu(I).[1, 13] Each class of ligand can facilitate the controlled polymerization of different monomers, with typically "active ligands" providing good control in polymerizing high k_p monomers (e.g. acrylates and acrylamides) and "less active" ligands achieving better control in the polymerization of low k_p monomers (e.g. methacrylates), where ligands typically have low lying π^* orbitals capable of accepting electrons from the metal stabilizing Cu(I).[9] However, it should be noted that active ligands have also been reported to mediate the polymerization of

methacrylates although no evidence of end group fidelity is provided.[14, 15] Finally, although solvent choice certainly has a much lower impact on radical polymerizations (in terms of both rate and stereochemistry) as opposed to ionic polymerizations, the choice of the reaction medium can still significantly affect the ATRP equilibrium and relevant rate constants.[9] Similar findings have also been observed in Cu(0)-mediated processes, where the results vary depending on the catalyst, ligand, solvent and monomer structure employed.[16] As such, it is necessary that all these components are judiciously matched (on top of adjusting other parameters such as temperature, dilutionor reaction time) depending on the targeted monomer type (e.g. acrylates, methacrylate, styrene etc.) in order to yield controlled polymerizations with high end group fidelity (Figure 1). In contrast, research in the area of RAFT polymerization has made more progress towards the development of universal chain transfer agents (CTAs), potentially due to the simpler overall system.[17-19]

Even after careful optimization of the reaction conditions of copper mediated ATRP, in order to maintain high end group fidelity one often has to stop the polymerization at moderate/low conversions (e.g. 60%) and extensively purify the macroinitiator product prior to performing a chain extension experiment which is a waste of materials and time consuming limiting commercial exploitation and attractiveness. In order to circumvent this, a number of different "variations" of ATRP and SET-LRP have recently been developed, including use of free radical initiators (initiators for continuous activator regeneration (ICAR) ATRP)[20], reducing agents (activators regenerated by electron transfer (ARGET) and AGET ATRP)[21, 22], electrochemical (eATRP)[23] and light stimuli (light ATRP),[24-30] as well as Cu(0)-wire and Cu(0) particle mediated processes.[31, 32] The latter two approaches have demonstrated high end group fidelity even at near-quantitative conversions as exemplified by the *in situ* synthesis of multiblock copolymers.[33-39] Moreover, to the best of our knowledge, *in situ* chain extensions with copper mediated polymerization approaches have only been reported for relatively high k_p monomers such as acrylates, as methacrylates are more susceptible to termination, chain transfer and side reactions. Importantly, all these techniques are capable of polymerizing specific families of monomers, however choosing the appropriate method depending on the targeted polymer can also be challenging.[12]

Considering these issues it becomes evident that tuning reaction conditions for different monomer classes can be challenging and time consuming. As such, a universal system where identical components (e.g. same initiator/ligand/solvent/catalyst) could be used for the controlled polymerization of a range of highly relevant monomers (e.g. acrylates, methacrylates, styrene) under environmentally friendly conditions would be highly desirable. More importantly, these polymers should exhibit not only narrow MWDs but also high end group fidelity, capable of facilitating the synthesis of block copolymers *in situ*. (Scheme 1) In addition, as many ligands used for classical ATRP or SET-LRP such as Me_6Tren or TPMA can be either expensive or require step-wise syntheses, utilizing commercially available and inexpensive ligands such as *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) would also be advantageous.

In order to address all of these features we report the controlled polymerization of acrylates, methacrylates and styrenics utilizing universal conditions (the same copper source, initiator, ligand and solvent). All the reagents are commercially available, inexpensive (e.g. PMDETA, copper source, solvent), "green" and easy to remove (isopropanol (IPA)) while the simple set up ensures accurate reproducibility. Under these carefully selected universal conditions acrylates, methacrylates and styrene can be successfully polymerized furnishing materials with high end group fidelity and narrow molecular weight distributions. Importantly, polymethacrylates and polystyrene can be successfully chain extended *in situ* upon sequential monomer addition forming diblock copolymers with low dispersities. This allows facile access to well-defined materials by both "experts" and non-experts for the first time.

EXPERIMENTAL

Materials

All materials were purchased from Sigma Aldrich or Fischer Scientific and used as received unless otherwise stated. All monomers were used without subsequent purification. HPLC IPA (99.9%) was used for all the experiments, including the chain extensions. *Tris*-(2-(dimethylamino)ethyl)amine (Me_6Tren) was synthesized according to previously reported literature and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) was distilled prior to use. Cu(0) (gauge 0.25 mm) wire was purchased from Comax Engineered wires and purified by immersion in conc. HCl for 15 minutes and subsequently rinsed with water and dried prior to use. ^{1}H NMR spectra were recorded on Bruker DPX-300 or DPX-400 spectrometers in $CDCl_3$. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane. Monomer conversions were determined via ^{1}H NMR spectroscopy by comparing the integrals of monomeric vinyl protons to polymer signals. ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz, equipped with a DCH ^{13}C-optimised cryoprobe. Size exclusion chromatography (SEC) measurements were conducted using an Agilent 390-LC MDS instrument fitted with differential refractive index (DRI), viscometry (VS), dual angle light scatter (LS) and two wavelength UV detectors. The system was equipped with two PLgel 5 mm mixed-C columns (300 x 7.5 mm), one PLgel 5 μm guard column and autosampler. Narrow linear poly(methyl methacrylate) and polystyrene standards (Agilent EasyVials) ranging from 200 to 1.0 x10^6 g mol^{-1} were used as calibrants. Samples were run at a flow rate of 1.0 mL min^{-1} at 30 °C. All samples were passed through a 0.22 μm GVHP membrane prior to analysis. The mobile phase was THF with 2% TEA and 0.01% BHT (butylated hydroxytoluene) additives. Experimental molar mass ($M_{n,\,SEC}$) and dispersity ($Đ$) values were analysed using Agilent GPC/SEC software (version 1.2). MALDI-ToF-MS was conducted using a

Bruker Daltonics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. Solutions in tetrahydrofuran (50 µL) of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propyldene] malonitrile (DCTB) or dithranol as a matrix (saturated solution), sodium iodide or sodium iodide as cationization agent (1.0 mg mL–1) and sample (1.0 mg mL^{-1}) were mixed, and 0.7 µL of the mixture was applied to the target plate. Spectra were recorded in reflector mode calibrating PEG-Me 1900 kDa.

Materials

General procedure for a typical Cu(0)-mediated RDRP of methyl methacrylate (MMA)

Methyl methacrylate (MMA) (4 mL or 3.76 g, 50 equiv.), pre-activated copper wire (5 cm), methyl-α-bromophenylacetate (MBPA) (0.119 mL or 0.171 g, 1 equiv.), $CuBr_2$ (8.35 mg, 0.05 equiv.) and IPA (4 mL) were added to a septum sealed vial, equipped with a stirring bar, around which the copper wire was wrapped. The mixture was subsequently deoxygenateddeoxygenated by bubbling with nitrogen for 20 min. PMDETA (0.057 mL, 0.36 equiv.) was then introduced in the vial via a gas-tight syringe and the polymerization was allowed to commence at 40 °C for 18 h. Samples were taken periodically under a nitrogen blanket and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ^{1}H NMR and SEC.

General procedure for a typical Cu(0)-mediated RDRP of styrene

Styrene (4 mL or 3.64 g, 50 equiv.), pre-activated copper wire (5 cm), MBPA (0.111 mL or 0.160 g, 1 equiv.), $CuBr_2$ (7.80 mg, 0.05 equiv.) and IPA (4 mL) were added to a septum sealed vial. The copper wire was wrapped around the stirrer bar and the mixture was subsequently deoxygenateddeoxygenated by bubbling with nitrogen for 20 min. PMDETA (0.052 mL, 0.36 equiv.) was then introduced in the vial via a gas-tight syringe and the polymerization was allowed to commence at 60 °C for 36 h. Samples were taken periodically under a nitrogen blanket and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ^{1}H NMR and SEC.

General procedure for a typical Cu(0)-mediated RDRP of methyl acrylate (MA)

MA (4 mL or 3.82 g, 50 equiv.), pre-activated copper wire (5 cm), MBPA (0.140 mL or 0.203 g, 1 equiv.), $CuBr_2$ (9.92 mg, 0.05 equiv.) and IPA (4 mL) were added to a septum sealed vial. The copper wire was wrapped around the stirrer bar and the mixture was subsequently deoxygenateddeoxygenated by bubbling with nitrogen for 20 min. PMDETA (0.033 mL, 0.18 equiv.) was then introduced in the vial via a gas-tight syringe and the polymerization was allowed to commence at 60 °C for 12 h. Samples were taken periodically under a nitrogen blanket and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ^{1}H NMR and SEC.

General procedure for a typical chain extension of PMMA with MMA

The general procedure for the homopolymerization of MMA by Cu(0)-mediated RDRP was followed, as given above. Homopolymer conversions were monitored by regular sampling to accurately determine the time at which near quantitative monomer conversion was reached according to ^{1}H NMR ($CDCl_3$). In subsequent experiments the homopolymerization of MMA was allowed to proceed for 8 h, prior to the addition of a mixture of freshly deoxygenated MMA (4 mL or 3.76 grams, 50 equiv.), IPA (4 mL) and PMDETA (0.057 mL, 0.36 equiv.). The polymerization was allowed to proceed at 40 °C for a further 18 h. Samples were taken under a nitrogen blanket and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ^{1}H NMR and SEC.

General procedure for a typical chain extension of PS with Styrene

The general procedure for the homopolymerization of styrene by Cu (0)-mediated RDRP was followed as given above. Homopolymer conversions were monitored by regular sampling to accurately determine the time at which full monomer conversion was reached according to ^{1}H NMR ($CDCl_3$). In subsequent experiments the homopolymerization of styrene was allowed to proceed for 36 h, before addition of a mixture of freshly deoxygenated styrene (8 mL or 7.28 grams, 50 equiv.), IPA (8 mL) and PMDETA (0.057 mL, 0.36 equiv.). The polymerization was allowed to proceed for a further 36 h at 60 °C. Samples were taken under a nitrogen blanket and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ^{1}H NMR and SEC.

General procedure for a typical chain extension of PMA with MA

PMA macroinitiator was synthesized according to the homopolymerization procedure, as given above. It was diluted in THF prior to filtration through a column of neutral alumina to remove dissolved copper salts. The polymer was isolated via precipitation in MeOH:H_2O (70% MeOH), and dried under vacuum. The degree of polymerization of the PMA was calculated by ^{1}H NMR ($CDCl_3$). The macroinitiator (0.73 g, DP_n = 58, 1 equiv.) was subsequently added to MA (1.13 mL, target DP_n = 50), pre-activated copper wire (5 cm), $CuBr_2$ (1.40 mg, 0.05 equiv.) and IPA (1.13 mL) in a septum sealed vial. The mixture was subsequently deoxygenated by purging with nitrogen for 15 min. PMDETA (0.0047 mL, 0.18 equiv.) was then introduced in the vial via a gas-tight syringe and the polymerization was allowed to commence at 60 °C. Samples were taken under a nitrogen blanket and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ^{1}H NMR and SEC.

RESULTS AND DISCUSSION

Methyl methacrylate, evaluating optimization towards universal conditions

Cu(0)-wire mediated polymerization is often employed for the controlled polymerization of acrylates (e.g. methyl acrylate) at ambient temperature often utilizing ethyl-α-bromoisobutyrate (EBiB) as the initiator, Me_6Tren as the ligand and DMSO as the solvent yielding poly(acrylates) with narrow molecular weight distributions and near-quantitative conversions.[40] A small amount of $CuBr_2$ deactivator is also typically added in order to improve the control over MWDs.[41] However, under identical conditions the polymerization of methyl methacrylate (MMA) leads to much slower polymerization rates reaching 77% conversion (overnight) with broad MWDs ($Đ \geq 1.5$) (Table 1, Entry 1 and Figure S1). Increasing the temperature to 40 °C gave no improvement over the conversion or the control over the MWD ($Đ \geq 1.76$), which demonstrates that this combination of initiator, solvent, ligand cannot facilitate the controlled polymerization of MMA (Table 1, Entry 2 and Figure S2). MBPA, a much less explored initiator,[42-44] exhibits high activity and should thus be suitable for methacrylates given they are considered active monomers.[9] Significantly, switching the initiator from EBiB to MBPA gave rise to low dispersities ($Đ$~1.15) although the conversion did not exceed 79% (overnight) even when the temperature was increased to 40 °C (Table 1, Entries 3-4 and Figure S3-S4). Regardless of the conversion, low dispersities clearly indicate that MBPA is an effective initiator for the controlled polymerization of methacrylates under Cu(0)-mediated conditions resulting in fast initiation with respect to propagation. As DMSO would not solubilize all our targeted polymers (polystyrene is insoluble in DMSO) we decided to search for an alternative solvent. At that point, we envisaged IPA as a potential candidate for two main reasons. Firstly, IPA has already been shown to facilitate the controlled polymerization of hydrophobic monomers (though only for acrylates) by forming a phase separation system (where monomer/catalyst are in a different from the polymer) with limited termination and side reactions.[45, 46] In addition, IPA is an inexpensive and "green" solvent,[47] which is easy to handle and can be removed by rotary evaporation (unlike DMSO).[48] However, switching the solvent from DMSO to IPA (Me_6Tren, MBPA

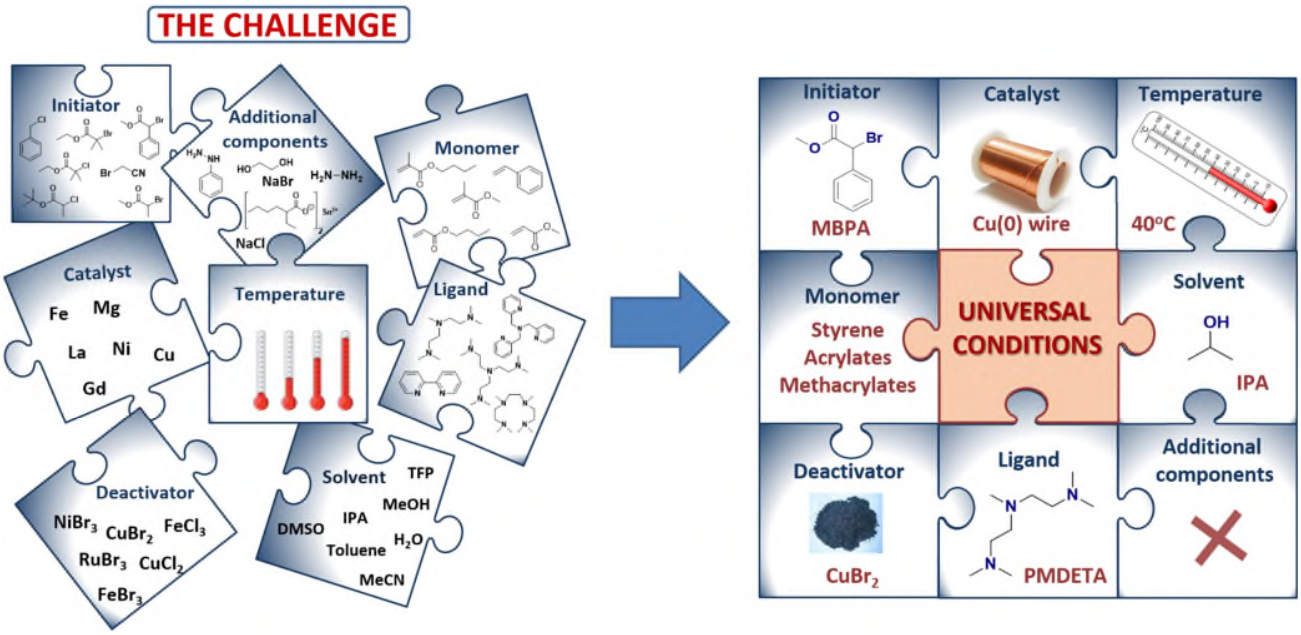

Figure 1: Schematic representation of the challenges typically encountered when conducting copper mediated polymerizations and our universal approach that can facilitate the polymerization of styrene, acrylates and methacrylates.

and temperature remaining the same) resulted in zero conversion being observed by either NMR or SEC, and increasing the temperature to 40 °C resulted in high dispersity polymer. ($Đ$ ~ 1.7) (Table 5, entries 5-6) and Figure S5). These results show that the combination of Me_6Tren with MBPA is unsuitable for the polymerization of methacrylates under the selected reaction conditions. Interestingly, when the ligand was changed from Me_6Tren to PMDETA (a less expensive alternative), narrow MWDs ($Đ$ ~ 1.16-1.18) could be obtained at either ambient or higher temperatures mirroring the results obtained from polymerizations in DMSO (where Me_6Tren was used instead of PMDETA, Table 1, Entry 7-8 and Figure S6-S7). Despite the success of these experiments, the final conversion was only 62% (after 18 h of reaction time) which precludes effective *in situ* chain extensions. In order to circumvent this, the concentration of the ligand was adjusted from 0.18 equiv. with re-

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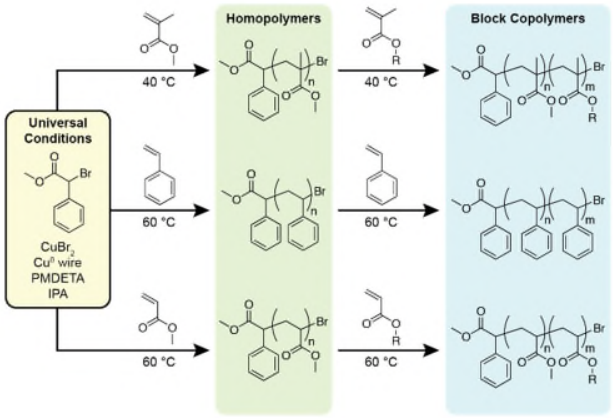
achieved if the reaction is ceased at lower conversions (e.g. $Đ$~ 1.10 at 93% of conversion, Table 1, Entry 10). However,

Entry Number	Initiator	Solvent	Ligand (% w.r.t [I])	Temp. (°C)	Conv. (%)	$M_{n,theory}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	$Đ$
1	EBiB	DMSO	Me_6Tren (18%)	RT	77	4100	7200	1.53
2	EBiB	DMSO	Me_6Tren (18%)	40	78	4200	6200	1.76
3	MBPA	DMSO	Me_6Tren (18%)	RT	79	4300	7800	1.15
4	MBPA	DMSO	Me_6Tren (18%)	40	62	3300	4600	1.26
5	MBPA	IPA	Me_6Tren (18%)	RT	<5	-	-	-
6	MBPA	IPA	Me_6Tren (18%)	40	25	1500	2500	1.68
7	MBPA	IPA	PMDETA (18%)	RT	57	3100	3800	1.16
8	MBPA	IPA	PMDETA (18%)	40	62	3300	4300	1.18
9	MBPA	IPA	PMDETA (36%)	40	98	5100	7000	1.18
10	EBiB	IPA	Me_6Tren (36%)	40	79	4200	5700	1.76
11	EBiB	IPA	PMDETA (36%)	40	99	5200	6200	1.43



Scheme 1: Universal conditions illustrating the synthesis of polyacrylate, polymethacrylate and polystyrene homo and block copolymers via Cu(0)-mediated RDRP

spect to the initiator to 0.36 equiv. It has been previously reported by Percec, Matyjaszewski and Haddleton that relatively small changes in ligand concentration can dramatically affect both the end group fidelity and the rate of the polymerization.[40, 49-52] Indeed the aforementioned change of ligand concentration resulted in a remarkable acceleration on the rate of the polymerization furnishing well-defined poly(MMA) with a final dispersity of 1.18 at near quantitative conversion (98%) (Table 1, entry 9, Figure S8-S9). It should be noted that even lower dispersities can be

as we were interested in the full capabilities of these universal conditions, including subsequent *in situ* chain extensions, all polymerizations were pushed to near-quantitative conversions. The isolated materials were then initially analyzed by MALDI-ToF-MS although no bromine could be detected attributed to MS fragmentation effects, in agreement with previous reports.[53, 54] (Figure S10) However, when quantitative ^{13}C NMR was measured 94% of C-Br end groups could be observed and thus showing very high end group fidelity under these conditions (Figures S11-12). In addition, ^{13}C NMR also showed similar stereochemistry (67% syndiotactic) in comparison to other ATRP analogues previously reported (Table S1 and Figure S13).[55] In order to further demonstrate the necessity to judiciously combine all the suggested components, MBPA was replaced by EBiB under our optimized conditions. However, broad MWDs were observed with either Me_6Tren or PMDETA, thus highlighting the importance of our optimized conditions (Table 1, Entries 11-12 and Figures S14-S15).

Investigating into the scope of the universal conditions; Different DPs, butyl and PEG methacrylate and block copolymers

In order to probe the potential of this system in maintaining control over higher molecular weights we conducted a range of polymerizations targeting degrees of polymerization from DP_n=50-400. Under identical conditions four poly(MMA) homopolymers were synthesized with MW varying from 7000

Table 1: ^{1}H NMR and SEC analysis of the polymerization of MMA, with optimization of solvent, ligand, temperature and ligand concentration shown.

to 42000 g mol^{-1}. In all cases ~90% conversion was reached with low dispersities ranging from 1.18 to 1.28 (Figures 2a and S16 and Table S2). In order to indirectly assess the end group fidelity of the system, *in situ* chain extensions of P(MMA with a second aliquot of MMA were also conducted furnishing higher MW polymer ($M_{n,sec}$=12800 g mol^{-1}) without any increase in the initial dispersity of the macroinitiator. As the conversion of the second block was ~84% we managed to further increase this by the addition of another aliquot of ligand (together with the monomer addition) which yielded an increased conversion (92%) (Figures S17-S18 and Table S3). Importantly, very little tailing in the low MW region was observed by SEC suggesting an efficient re-initiation of PMMA and high end group fidelity under the selected conditions. The scope of the system was subsequently extended to include butyl methacrylate (BMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMA) in order to illustrate the ability to facilitate the controlled polymerization of both hydrophobic and hydrophilic monomers. Pleasingly, the polymerization of the hydrophilic PEGMA led to narrow MWDs ($Đ$~1.11) at near quantitative conversion (~99%) with a final M_n of 27600 g mol^{-1} (Figures S19-S20 and Table S4). Butyl methacrylate was also successfully polymerized to afford a homopolymer with low dispersity ($Đ$~1.22) at ~97% of conversion (Figures S21-S22 and Table S4). The latter monomer (BMA) was also employed to *in situ* chain extend a poly(MMA) macroinitiator yielding a well-defined poly(MMA)-*b*-poly($_{BMA}$) diblock copolymer with a final dispersity of 1.20 and a final M_n of 17200 g mol^{-1} (Figures 2b and S23 and Table S5). Again, it should be noted that the conversion of the second block was also pushed to near-completion (~99%) with earlier samples yielding even lower dispersities. Overall, these results demonstrate that the combination of MBPA, IPA, PMDETA and Cu(0) wire can successfully mediate the controlled polymerization of either hydrophobic or hydrophilic methacrylates yielding low dispersed polymers even at very high conversions leading to the *in situ* synthesis of well-defined diblock copolymers.

The synthesis of well controlled poly(styrene) under universal conditions

In the previous section the controlled polymerization of methacrylates was demonstrated under the following conditions: [MMA]:[MBPA]:[PMDETA]:[$CuBr_2$] = [50]:[1]:[0.36]:[0.05] in 1:1 (v/v) monomer to solvent (IPA) ratio at 40 °C. However, when identical conditions were utilized to polymerize styrene, no conversion was detected by ^{1}H NMR spectroscopy or SEC (Table 2, entry 1). It is interesting to note how one set of conditions provide quantitative conversions, high end group fidelity and low dispersities for one monomer family (methacrylates) but give rise to no conversion for another family of monomer (styrene), further demonstrating the need for universal conditions. Significantly, by simply raising the temperature from 40 °C to 60 °C we obtained a well-defined poly(styrene) exhibiting narrow molecular weight distributions ($Đ$~ 1.15) for up to 98% conversion (Table 2, Entry 2 and Figures 2c and S24-S25). It is noted that with lower ligand concentration (0.18 equiv. with respect to the initiator) a slower polymerization was detected reaching only ~ 58% of conversion under the same time scale of polymerization (Figure S26). Thus, for both methacrylates and styrene, increasing the ligand concentration from 0.18 to 0.36 equiv. results in a largee increase of the conversion without compromising the MWDs (Table 2, entry 3).

Although the polymerization rate was low, requiring ~36 h to reach completion, high end group fidelity could be maintained throughout the reaction as evident by *in situ* chain extensions. Note however that similarly to previous reports, the MALDI-ToF mass spectrometry showed an absence of a bromine, but instead a double bond terminated polymer which is attributed to the loss of HBr during the ionization of the silver

Table 2: ^{1}H NMR and SEC analysis of the polymerization of polystyrene (DP50) via Cu(0)-RDRP, with optimisation of temperature and ligand concentration shown.

Entry Number	Ligand (% w.r.t [I])	Temp. (°C)	Conv. (%)	$M_{n,theory}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	$Đ$
1	PMDETA (18%)	40	0	-	-	-
2	PMDETA (18%)	60	58	3200	4100	1.16
3	PMDETA (36%)	60	98	5300	8100	1.15

Table 3: ^{1}H NMR and SEC analysis for the polymerization of methyl acrylate, with optimization of solvent, ligand, temperature and ligand concentration shown.

Entry Number	Initiator	Solvent	Ligand (% w.r.t [I])	Temp. (°C)	Conv. (%)	$M_{n,theory}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	$Đ$
1	EBiB	DMSO	Me_6Tren (18%)	RT	>99.9	4500	5700	1.06

2	EBiB	IPA	Me_6Tren (18%)	RT	93	4200	5100	1.10
3	MBPA	IPA	Me_6Tren (18%)	RT	0%	-	-	-
4	MBPA	IPA	PMDETA (36%)	RT	5%	-	-	-
5	MBPA	IPA	PMDETA (36%)	40	10%	-	-	-
6	MBPA	IPA	PMDETA (36%)	60	88	4000	5200	1.28
7	MBPA	IPA	PMDETA (18%)	60	90	4100	4600	1.15

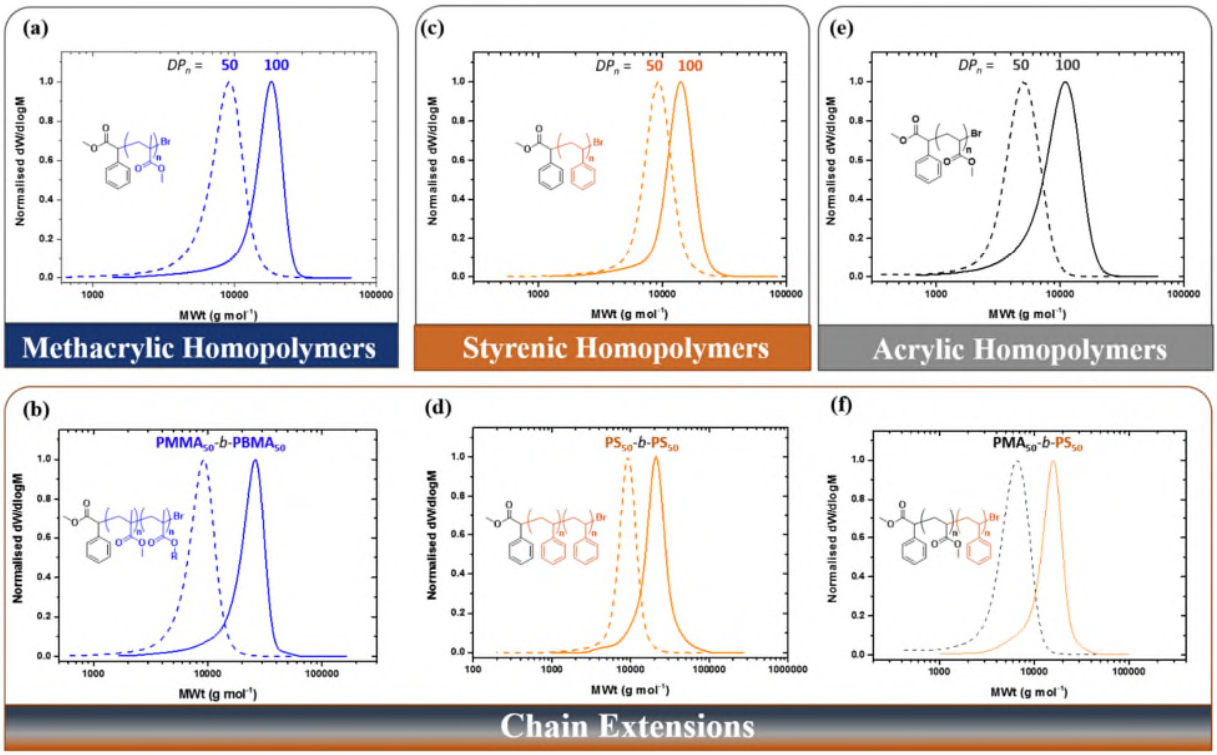


Figure 2: Methacrylic, styrenic and acrylic homo and block copolymers synthesized via Cu(0)-mediated RDRP showing SEC traces of a) PMMA (DP_n =50-100) b) *in situ* block copolymer PMMA-PBMA c) PS (DP_n =50-100) d) *In situ* chain extension of PS e) PMMA (DP_n =50-100) f) PMA (DP_n =50-100) b) block copolymer PMMA-PBMA.

salt.[56, 57] (Figure S27) In order to further investigate the presence of an active end group, a polystyrene homopolymer (98% conversion, $M_{n,SEC}$~8100 g mol^{-1}, $Đ$~ 1.15) was chain extended with another aliquot of styrene and an additional aliquot of PMDETA (consistent with the chain extension of MMA) resulting in a clear shift in the MWs by SEC and a final M_n of 17700 g mol^{-1} demonstrating high end group fidelity and low dispersity values (final $Đ$~ 1.24) (Figures 2d and S28, and Table S6). As PEO diblocks are highly desirable for many applications,[58-60] we were also interested in synthesizing a PEG macroinitiator functionalized with MBPA (Figures S29-S30). Pleasingly, a clear shift to higher molecular weight was observed upon addition of styrene yielding a final diblock copolymer with dispersity as low as 1.17, thus showing that poly(ethylene oxide)-*b*-polystyrene can be synthesized under the universal conditions (Figure S31). Higher MW polystyrene could also be obtained (DP_n=100), with a final M_n of ~12000 g mol^{-1} and dispersity as low as 1.17 (Figure 2c and Table S7). These results show that under the universal conditions both methacrylates and styrene can be successfully polymerized yielding low dispersity polymers, with near quantitative conversions and high end group fidelity, capable of undergoing *in situ* chain extensions and block copolymerizations.

The synthesis of well controlled poly(acrylates) under universal conditions

Our next target was to examine the polymerization of acrylates. Arguably, the controlled polymerization of acrylates is well documented in the literature with either Cu(0) or CuBr mediated systems presenting impressive end group fidelity as exemplified by the synthesis of multiblock copolymers.[61] EBiB or methyl-bromopropionate (MBP), Me_6Tren and DMSO at ambient temperature are well-known as "ideal" conditions to polymerize MA. Under

these conditions, and in agreement with the literature, >99% conversion in a few hours can be achieved with dispersities as low as 1.06 (Table 3, Entry 1, Figure S32).[35, 62, 63] However, having a universal set of conditions and reagents that would allow for the controlled polymerization of acrylates, methacrylates and styrene would be advantageous as it enables greater accessibility of polymeric materials by non-experts. As such, we were initially interested to explore whether IPA could afford the controlled polymerization of MA (maintaining EBiB and Me_6Tren). As anticipated, the good control over the MWDs was maintained ($Đ$~ 1.10) with the reaction reaching >90% conversion (Table 3, Entry 2 and Figure S33). Nevertheless, EBiB was subsequently switched to MBPA (maintaining IPA, Me_6Tren and ambient temperature) but no conversion was observed under these conditions further highlighting how the change of just one component can have detrimental effects on the polymerization (Table 3, Entry 3). Switching the ligand from Me_6Tren to PMDETA (0.36 equiv. with respect to the initiator) did not improve the outcome and no polymer was obtained (Table 4, Entry 4). However, when the temperature was raised from ambient temperature to 60 °C the polymerization occurred yielding 88% of conversion and a dispersity of 1.28 (Table 3, Entries 5 and 6 and Figure S34). Once more, it is quite remarkable how a small change in the temperature could switch the polymerization "on". As it has already been reported that acrylates possess higher end group fidelity at lower ligand concentrations, the amount of PMDETA was subsequently decreased from 0.36 equiv. to 0.18 equiv. (with respect to the initiator) resulting in a decrease in the dispersity from 1.28 to 1.15, whilst also presenting high conversion (~90%) (Table 3, Entry 7 and Figures 2e and S35-S36). This result shows that methyl acrylate can also be successfully polymerized under the universal conditions utilizing the inexpensive and commercially available ligand PMDETA, the more environmentally friendly solvent IPA (in comparison to DMSO), MBPA as the initiator and ppm concentrations of copper. Higher molecular weights of poly(MA) could also be obtained (DP=100) although the dispersity value increased from 1.15 to 1.30 (Figure 2e and Table S8). Nevertheless, butyl acrylate was also successfully polymerized with a dispersity of 1.28 at ~89% of conversion demonstrating the capability of the system to polymerize various acrylates (Figures S37-38 and Table S9).

As conversions for the poly(acrylates) did not reach quantitative or near quantitative levels, *in situ* chain extensions were not attempted. However, MALDI-ToF-MS analysis revealed very high end group fidelity with the major polymer peak distribution corresponding to bromine terminated poly(MA) (Figure 3). As such, the poly(MA) was isolated and purified (Figure S39) prior to addition of another aliquot of MA and this resulted in a near complete shift of the initial macroinitiator peak on analysis by SEC ($Đ$~1.27 at ~90% conversion for the chain extension, Figures S40-S41 and Table S10). It is noted that a low MW shoulder was evident suggesting that the polymerization of acrylates is not ideal under these conditions and 100% end group fidelity cannot be maintained. Similar results were obtained when poly(MA) was chain extended with butyl acrylate (Figures S42-S43 and Table S11).

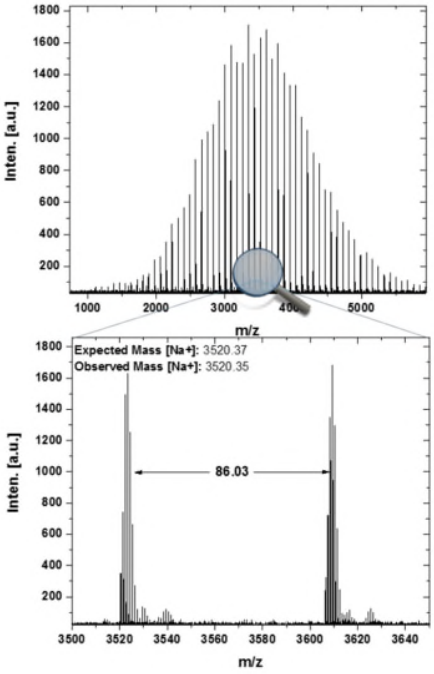


Figure 3: MALDI-ToF-MS spectra of PMA synthesized via Cu(0)-RDRP

In addition, when poly(MA) was chain extended with styrene, more efficient re-initiation was observed furnishing a well-defined diblock poly(MA)-b-polystyrene copolymer with $Đ$~1.21 and $M_{n,SEC}$ ~ 12200 g mol^{-1} (Figures 2f and S44, and Table S12). The same poly(MA) macroinitiator could also be chain extended with a larger aliquot of styrene forming higher MW diblock copolymers of $M_{n,SEC}$ = 19900 g mol^{-1} and $Đ$~1.24 (Figure S45 and Table S12). This is a significant achievement as it demonstrates that cross propagation is also possible in our system despite the poly(acrylates) being under not typically ideal conditions. As such, all the monomer families selected could be effectively polymerized under the universal conditions exhibiting in all cases good control over MWDs, high conversions and high end group fidelity.

CONCLUSIONS

We report the efficacious and controlled polymerization of acrylates, methacrylates and styrene under one set of universal reaction conditions yielding well-defined materials with low dispersities and high end group fidelity at near quantitative conversions. *In situ* chain extensions and block copolymerizations afforded the synthesis of low dispersity diblock copolymers for the case of methacrylates and styrene while isolation of the poly(MA) macroinitiator also yielded well defined diblocks when styrene was used as the second monomer. All three monomers utilized MBPA as the initiator, PMDETA as the ligand, IPA as the solvent, Cu(0) wire as the copper source and $CuBr_2$ as deactivator. Importantly all the materials employed are commercially available and inexpensive while the solvent used (IPA) is environmentally friendly and the Cu(0) catalyst

used is in ppm levels. By employing one set of conditions for the controlled polymerization of broadly applicable monomer families with standard, readily available reagents, this will allow facile access to advanced polymeric materials for all researchers.

ASSOCIATED CONTENT

Supporting Information.
Further detailed experimental and supplementary figures available free of charge via the Internet at http://pubs.acs.org.

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Notes

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