

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

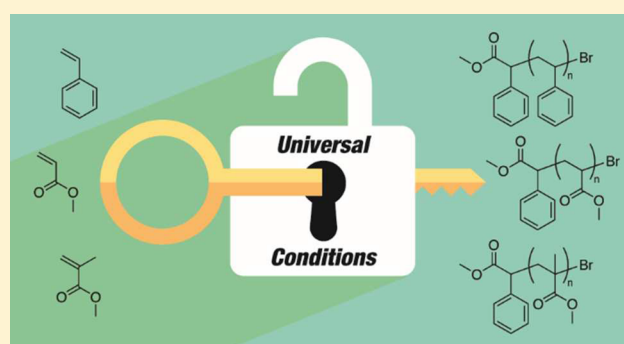
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S Supporting Information

ABSTRACT: Atom transfer radical polymerization (ATRP) typically requires various parameters to be optimized in order to achieve a high degree of control over molecular weight and dispersity (such as the type of initiator, transition metal, ligand, solvent, temperature, deactivator, added salts, and reducing agents). 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 nonexperts as choosing the appropriate conditions for successful polymerization can be time-consuming and overall an arduous task. In this work, we describe one set of universal conditions for the efficacious polymerization of acrylates, methacrylates and styrene (using an identical initiator, ligand, copper salt, and solvent) based on commercially available and inexpensive 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. Among 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^{6–11} (typically referred to as either single electron transfer (SET)-LRP or supplemental activation and reducing agents (SARA)-ATRP) have significantly contributed to this field.¹²

Both ATRP and Cu(0)-RDRP are considered as multi-component 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., CuBr₂, CuCl₂, 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 toward 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.^{13–15} The selection of a suitable catalyst is also of importance as different reactivities can lead to vastly different rates of polymerization (k_p), thus compromising overall control.¹⁶ 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 (Me₆Tren)) to very low activity (bipyridine (bpy), tetramethylethylenediamine (TMEDA)), where high activity corresponds to the ligands ability to stabilize Cu(II) relative to Cu(I).^{15–17} 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

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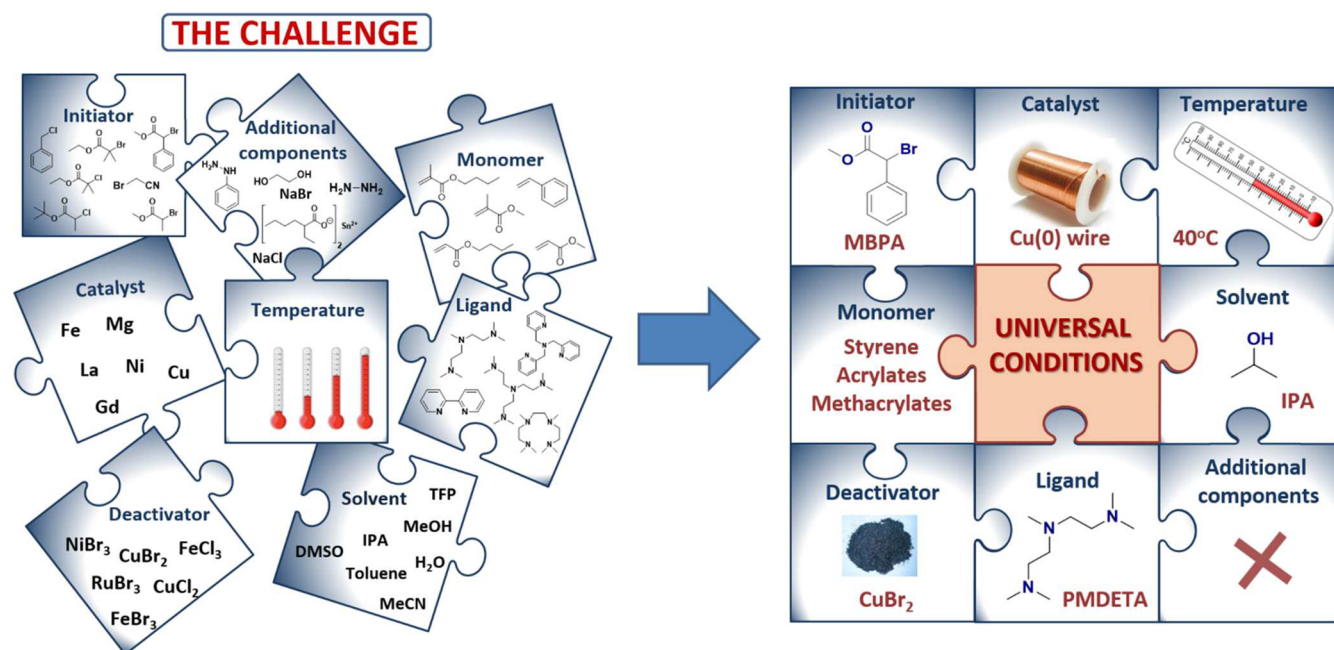


Figure 1. Schematic representation of the challenges typically encountered when conducting copper mediated polymerizations and our universal approach that can facilitate the polymerization of styrene, acrylates, and methacrylates.

low lying π^* orbitals capable of accepting electrons from the metal stabilizing Cu(I).¹³ 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.^{18,19} 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.¹³ Similar findings have also been observed in Cu(0)-mediated processes, where the results vary depending on the catalyst, ligand, solvent, and monomer structure.²⁰ As such, it is necessary that all these components are judiciously matched (on top of adjusting other parameters such as temperature, dilution or 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 toward the development of universal chain transfer agents (CTAs), potentially due to the simpler overall system.^{21–23}

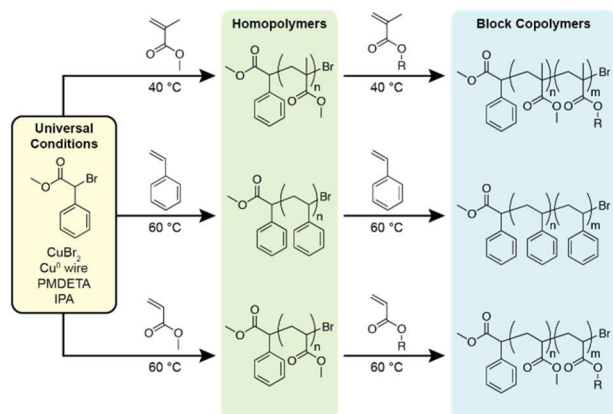
Even after careful optimization of the reaction conditions of copper mediated ATRP, in order to maintain high end group fidelity one often has to stop the polymerization at moderate/low conversions (e.g., 60%) and extensively purify the macroinitiator product prior to performing a chain extension experiment 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 have recently been developed, including use of free radical initiators (initiators for continuous activator regeneration (ICAR) ATRP),²⁴ reducing agents (activators regenerated by electron transfer (ARGET) and AGET ATRP),^{25,26} electrochemical (eATRP),²⁷ and light stimuli (light ATRP),^{28–34} as well as Cu(0)-wire and Cu(0) particle-mediated processes.^{35,36} 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.^{37–43} 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 exhibit much lower propagation rates. 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.¹⁶

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, and 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 Me₆Tren or TPMA can be either expensive or require stepwise 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 styrene 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 setup 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

Scheme 1. Universal Conditions Illustrating the Synthesis of Polyacrylate, Polymethacrylate, and Polystyrene Homo and Block Copolymers via Cu(0)-Mediated RDRP



sequential monomer addition forming diblock copolymers with low dispersities. This allows facile access to well-defined materials by both “experts” and nonexperts for the first time.

RESULTS AND DISCUSSION

Methyl Methacrylate, Evaluating Optimization toward Universal Conditions. Cu(0)-wire mediated polymerization is frequently employed for the controlled polymerization of acrylates (e.g., methyl acrylate) at ambient temperature often utilizing ethyl α -bromoisobutyrate (EBiB) as the initiator, Me₆Tren as the ligand and DMSO as the solvent yielding poly(acrylates) with narrow molecular weight distributions and near-quantitative conversions.⁴⁴ A small amount of CuBr₂ deactivator is also typically added to improve the control over MWDs.⁴⁵ However, under identical conditions, the polymerization of methyl methacrylate (MMA) leads to much slower polymerization rates reaching 77% conversion (overnight) with broad MWDs ($\bar{D} \geq 1.5$) (Table 1, Entry 1 and Figure S1 of the Supporting Information, SI). Increasing the temperature to 40 °C gave no improvement over the conversion or the control over the MWD ($\bar{D} \geq 1.76$), which demonstrates that this combination of initiator, solvent, and ligand cannot facilitate the controlled polymerization of MMA (Table 1, Entry 2 and Figure S2). MBPA, a much less explored

initiator,^{46–48} which exhibits high activity and should thus be suitable for polymerizing methacrylates given they are considered active monomers.¹³ Significantly, switching the initiator from EBiB to MBPA gave rise to low dispersities ($\bar{D} \approx 1.15$) although the conversion did not exceed 79% (overnight) even when the temperature was increased to 40 °C (Table 1, Entries 3–4 and Figures S3 and 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. First, 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 layer to the polymer) with limited termination and side reactions.^{49,50} In addition, IPA is an inexpensive and “green” solvent,⁵¹ which is easy to handle and can be removed by rotary evaporation (unlike DMSO).⁵² However, switching the solvent from DMSO to IPA (Me₆Tren, MBPA 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. ($\bar{D} \approx 1.7$) (Table 1, entries 5–6 and Figure S5). These results show that the combination of Me₆Tren with MBPA is unsuitable for the polymerization of methacrylates under the selected reaction conditions. Interestingly, when the ligand was changed from Me₆Tren to PMDETA (a less expensive alternative), narrow MWDs ($\bar{D} \approx 1.16$ –1.18) could be obtained at either ambient or higher temperatures mirroring the results obtained from polymerizations in DMSO (where Me₆Tren was used instead of PMDETA, Table 1, Entries 7–8 and Figures S6 and 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 respect 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.^{44,53–56}

Table 1. ¹H NMR and SEC Analysis of the Polymerization of MMA, with Optimization of Solvent, Ligand, Temperature and Ligand Concentration Shown^a

entry number	initiator	solvent	ligand (% w.r.t [I])	temp. (°C)	conv. (%)	$M_{n,theory}$	$M_{n,SEC}$	\bar{D}
1	EBiB	DMSO	Me ₆ Tren (18%)	RT	77	4100	7200	1.53
2	EBiB	DMSO	Me ₆ Tren (18%)	40	78	4200	6200	1.76
3	MBPA	DMSO	Me ₆ Tren (18%)	RT	79	4300	7800	1.15
4	MBPA	DMSO	Me ₆ Tren (18%)	40	62	3300	4600	1.26
5	MBPA	IPA	Me ₆ Tren (18%)	RT	<5			
6	MBPA	IPA	Me ₆ Tren (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	MBPA	IPA	PMDETA (36%)	40	90	4700	6900	1.13
11	EBiB	IPA	Me ₆ Tren (36%)	40	79	4200	5700	1.76
12	EBiB	IPA	PMDETA (36%)	40	99	5200	6200	1.43

^aIn all polymerizations, 5 cm of Cu(0) wire and 5% CuBr₂ with respect to initiator were utilized, and samples were taken after 18 h. The volume ratio of monomer to solvent was maintained at 1:1 throughout. The target DP was 50 and conversion was calculated via ¹H NMR.

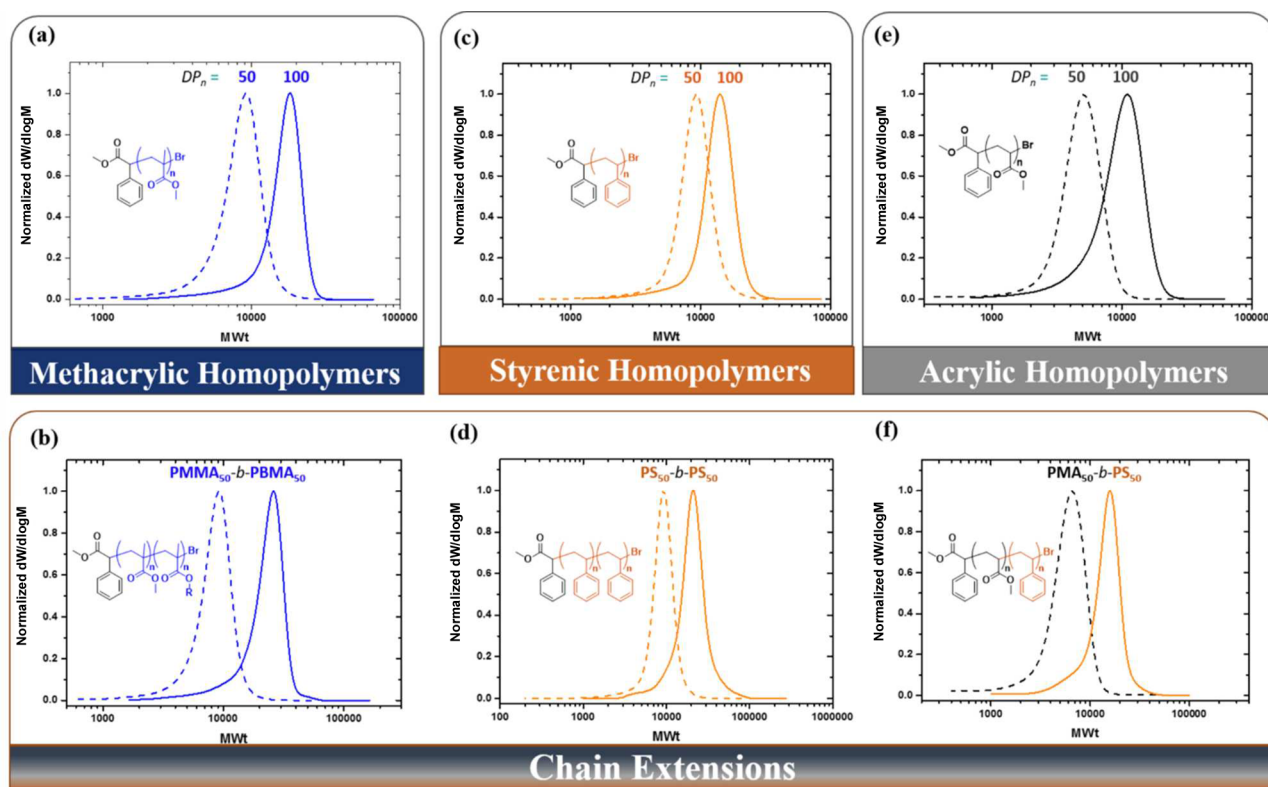


Figure 2. Methacrylic, styrenic, and acrylic homo and block copolymers synthesized via Cu(0)-mediated RDRP showing SEC traces of (a) PMMA ($DP_n = 50$ – 100); (b) in situ block copolymer PMMA–PBMA; (c) PS ($DP_n = 50$ – 100); (d) in situ chain extension of PS; (e) PM ($DP_n = 50$ – 100); and (f) block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

Indeed the aforementioned change of ligand concentration resulted in a remarkable acceleration on the rate of the polymerization furnishing well-defined PMMA with a final dispersity of 1.18 at near quantitative conversion (98%) (Table 1, entry 9, Figures S8 and S9). It should be noted that even lower dispersities can be achieved if the reaction is ceased at lower conversions (e.g., $\bar{D} \approx 1.13$ at 93% of conversion, Table 1, Entry 10). However, 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^{57,58} (Figure S10). However, when quantitative ¹³C NMR was measured 94% of C–Br end groups could be observed, thus showing very high end group fidelity under these conditions (Figures S11–12). In addition, ¹³C NMR also showed similar stereochemistry (67% syndiotactic) in comparison to other ATRP analogues previously reported (Table S1 and Figure S13).⁵⁹ 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 Me₆Tren or PMDETA, thus highlighting the importance of our optimized conditions (Table 1, Entries 11–12 and Figures S14–S15).

Investigating the Scope of the Universal Conditions; Different DP_n, 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 PMMA homopolymers were synthesized with molecular weight (MWt) varying from 7000 to 42 000. 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 PMMA with a second aliquot of MMA were also conducted furnishing higher MWt polymer ($M_{n,sec} = 12\ 800$) 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 MWt region was observed by SEC suggesting an efficient reinitiation 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 ($\bar{D} \approx 1.11$) at near quantitative conversion (~99%) with a final M_n of 27 600 (Figures S19–S20 and Table S4). Butyl methacrylate was also successfully polymerized to afford a homopolymer with low dispersity ($\bar{D} \approx 1.22$) at ~97% of conversion (Figures S21–S22 and Table S4). The latter monomer (BMA) was also employed to in situ chain extend a PMMA macroinitiator yielding a well-defined p(MMA)-*b*-p(BMA) diblock copolymer with a final dispersity of 1.20 and a final M_n of 17 200 (Figures 2b and S23 and Table

Table 2. ^1H NMR and SEC Analysis of the Polymerization of Polystyrene (DP50) via Cu(0)-RDRP, with Optimization of Temperature and Ligand Concentration Shown^a

entry number	ligand (% w.r.t [I])	temp. (°C)	conv. (%) [*]	$M_{n,\text{theory}}$	$M_{n,\text{SEC}}$	\bar{D}
1	PMDETA (18%)	40	0			
2	PMDETA (18%)	60	58	3200	4100	1.16
3	PMDETA (36%)	60	98	5300	8100	1.15

^aIn all polymerizations, 5 cm of Cu(0) wire and 5% CuBr₂ with respect to initiator were utilized, and samples were taken after 36 h. The volume ratio of monomer to solvent was maintained at 1:1 throughout. The target DP was 50 and conversion was calculated via ^1H NMR.

Table 3. ^1H NMR and SEC Analysis for the Polymerization of Methyl Acrylate, with Optimization of Solvent, Ligand, Temperature, and Ligand Concentration Shown^a

entry number	initiator	solvent	ligand (% w.r.t [I])	temp. (°C)	conv. (%) [*]	$M_{n,\text{theory}}$	$M_{n,\text{SEC}}$	\bar{D}
1	EBiB	DMSO	Me ₆ Tren (18%)	RT	>99.9	4500	5700	1.06
2	EBiB	IPA	Me ₆ Tren (18%)	RT	93	4200	5100	1.10
3	MBPA	IPA	Me ₆ Tren (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

^aIn all polymerizations, 5 cm of Cu(0) wire and 5% CuBr₂ with respect to initiator were utilized, and samples were taken after 18 h. The volume ratio of monomer to solvent was maintained at 1:1 throughout. The target DP was 50 and conversion was calculated via ^1H NMR.

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.

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]:[CuBr₂] = [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 ^1H 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 to 60 °C, we obtained well-defined poly(styrene) exhibiting a narrow molecular weight distribution ($\bar{D} \approx 1.15$) at 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 large increase in 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 salt^{60,61} (Figure S27). To demonstrate the presence of an active end group, a polystyrene homopolymer (98% conversion, $M_{n,\text{SEC}} \approx 8100$, $\bar{D} \approx 1.15$) 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 MWt by SEC and a final M_n of 17 700 demonstrating high end group fidelity and low dispersity values (final $\bar{D} \approx 1.24$) (Figures 2d and S28 and Table S6).

As PEO diblocks are highly desirable for many applications,^{62–64} we were also interested in synthesizing a PEG macroinitiator functionalized with MBPA (Figures S29 and 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 molecular weight polystyrene could also be obtained ($DP_n = 100$), with a final M_n of ~12 000 and dispersity as low as 1.17 (Figure 2c and Table S7). These results show that under 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.

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.⁶⁵ EBiB or methyl-bromopropionate (MBP), Me₆Tren, 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).^{39,66,67} 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 nonexperts. As such, we were initially interested to explore whether IPA could afford the controlled polymerization of MA (maintaining EBiB and Me₆Tren). As anticipated, the good control over the MWDs was maintained ($\bar{D} \approx 1.10$) with the reaction reaching >90% conversion (Table 3, Entry 2 and Figure S33). Nevertheless, EBiB was subsequently switched to MBPA (maintaining IPA, Me₆Tren, 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 Me₆Tren to PMDETA (0.36 equiv. with respect to the initiator) did not improve the outcome and no polymer was obtained (Table 3, 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, while also presenting a higher 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 PMA 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 and 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 PMA 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 ($\bar{D} \approx 1.27$ at ~90% conversion for the chain extension, Figures S40 and S41 and Table S10). Similar results were obtained when PMA was chain extended with butyl acrylate (Figures S42 and S43 and Table S11). In addition, PMA was chain extended with styrene, furnishing a well-defined diblock poly(MA)-*b*-polystyrene copolymer with $\bar{D} \approx 1.21$ and $M_{n,SEC} \approx 12\,200$ (Figures 2f and S44, and Table S12). The same PMA macroinitiator could also be chain extended with a larger aliquot of styrene forming higher MWt diblock copolymers of $M_{n,SEC} = 19\,900$ and $\bar{D} \approx 1.24$ (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 of 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.

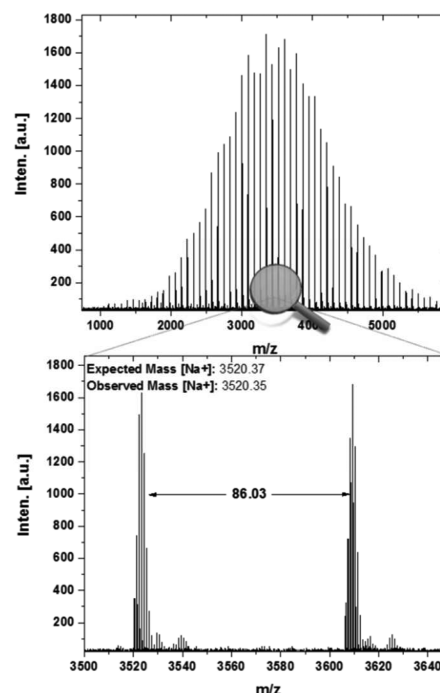


Figure 3. MALDI-ToF-MS spectra of PMA synthesized via Cu(0)-RDRP.

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 at near quantitative conversions. High end group fidelity was also demonstrated by successful chain extension from PMMA, PS, and PMA macroinitiators generating a range of diblocks without compromising the control over the molecular weight distributions. All polymerizations utilized MBPA as the initiator, PMDETA as the ligand, IPA as the solvent, Cu(0) wire as the copper source, and CuBr₂ 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. Employing one set of conditions for the controlled polymerization of three broadly applicable monomer families while utilizing readily available reagents, will allow facile access to advanced polymeric materials for all researchers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11783.

Further detailed experimental including general procedures for all syntheses and supplementary figures (PDF)

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Notes

The authors declare no competing financial interest.

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