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Highly Efficient Atom Transfer Radical Polymerization System Based on the SaBOX/Copper Catalyst

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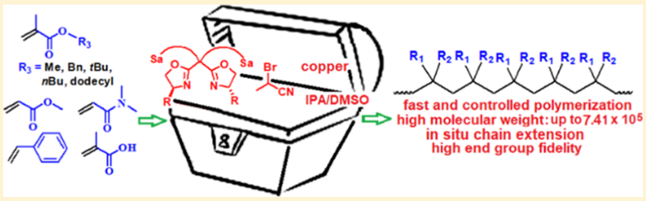
Supporting Information

ABSTRACT: A side-armed bis(oxazoline) (SaBOX)/copper catalyst, possessing a low equilibrium constant ($K_{ATRP} = k_{act}/k_{deact}$) and bearing large side-arm groups, was employed for supplemental activation and reducing agent atom transfer radical polymerization (SARA ATRP) of methyl methacrylate (MMA), which suppressed radical−radical termination events and successfully achieved very fast and controlled polymerizations, high end group fidelity, and ultrahigh molecular weight (up to 741 kg/mol) under common conditions. Compared with the copper complex bearing pentamethyldiethylenetriamine or tris[2-(dimethylamino)ethyl]amine (Me_6TREN) as the ligand, the SaBOX/copper catalyst performed much better in terms of polymerization rate and controllability under the same conditions via lowering the growing radical concentration and prolonging the time scale of living polymerization, an indicative of its unprecedentedly high efficiency in ATRP of MMA. The versatility and robustness of the SaBOX/copper system was further demonstrated by the controlled polymerization of various monomers, such as methacrylates, acrylates, styrenes, acrylamide, and even methacrylic acid. In situ chain extension experiments confirmed the very high end group fidelity, allowing the convenient preparation of well-defined block copolymers.



■ INTRODUCTION

As a powerful tool for synthesis of polymers with almost perfect control over molecular weight (MW) and topology, atom transfer radical polymerization (ATRP) is highly attractive across laboratories, disciplines, and levels of chemical expertise.[1−10] However, the simultaneous achievement of excellent controllability, high efficiency, and high MW (≥100 kg/mol) has been considered a great challenge in ATRP, especially for low k_p monomers, such as methyl methacrylate (MMA). This is due to the unavoidable and irreversible radical−radical termination events, which become prominent with the increase of MW and relative concentration of the radical to the monomer. In order to achieve excellent controllability, it is necessary to slow down polymerization (reduce radical concentration), limit conversion, and/or target lower degree of polymerization (DP).[11−13] It is difficult to efficiently realize ultrahigh and controlled MW in ATRP of MMA under common conditions.[14−21] As previously reported, with DP_{target} = 10 000 in activators generated by electron transfer ATRP of MMA at 1 atm, the conversion was only 16% in 40 h, and the resultant polymer possessed a number-average molar mass (M_n) of 215 kg/mol and a broad MW distribution of 2.02.[14] Besides, one often has to stop the polymerization at moderate/low conversions (e.g., 60%) to maintain high end group fidelity and extensively purify the macroinitiator product prior to performing a chain extension experiment.[22−24]

We envisioned that the employment of the catalytic system possessing relatively low K_{ATRP} could lower the growing radical concentration and suppress radical−radical termination and thus prolong the time scale of living polymerization and achieve highly productive polymerization (i.e., high efficiency). In addition, we anticipated that the optimization of ligands based on the “side arm strategy”[25,26] will have a great consequence on the efficiency and controllability of ATRP. By this way, we developed a highly efficient system with excellent controllability to conquer the challenging problems aforementioned. It was achieved by combining $CuBr_2$ with side-armed bis(oxazoline) (SaBOX) ligands[27−31] (Scheme 1) that are successfully applied in asymmetric catalysis. Herein, we wish to report the relevant research results in detail.

■ RESULTS AND DISCUSSION

Effects of the Ligand on SARA ATRP of MMA. We initially utilized 2-bromopropionitrile (BPN) as the initiator

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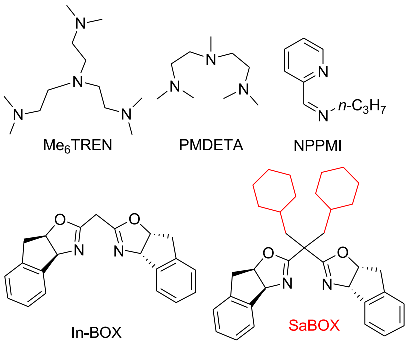
Scheme 1. Ligands Involved in This Work



and dimethyl sulfoxide (DMSO) as the solvent under similar conditions, which were frequently employed for the Cu(0)-mediated polymerization of acrylates at ambient temperature by aliphatic amine ligands.[32,33] By employing SaBOX as the ligand, we are pleased to find that the polymerization of MMA with a DP$_{target}$ of 100 was very fast and reached 86% conversion in 2.4 h with a narrow MW distribution (MWD, $Đ$ = 1.22, run 1 in Table 1). In contrast, the complexes with pentamethyldiethylenetriamine (PMDETA) and Me$_6$TREN as ligands afforded much lower conversions (<10%) and much broader MWD ($Đ$ > 3.0) under the same conditions (runs 2−3). These results demonstrated that SaBOX was more efficient than PMDETA or Me$_6$TREN as the ligand under current conditions. Besides, the similar comparison results were obtained from the polymerizations employing ethyl α-bromoisobutyrate (EBiB) or ethyl α-bromophenylacetate (EBPA) as the initiator instead of BPN (Table S1). Furthermore, the initiation by EBiB or EBPA led to less controlled polymerizations than that by BPN in the SaBOX/copper system, as the MWs were more broadly distributed ($Đ$ = 1.52−1.59) and the experimental MW values more deviated from the theoretical ones.

Table 1. SARA ATRP of MMA Employing Different Ligands[a]

run	ligand	t (h)	conv.[b] (%)	$M_{n,theory}$ (kg/mol)	$M_{n,GPC}$ (kg/mol)	$Đ$
1	SaBOX	2.4	86	8.7	14.8	1.22
2	PMDETA	2.4	9.1	1.0	133.6	3.07
3	Me$_6$TREN	2.4	4.8	0.6	40.5	3.26
4	NPPMI	2.4	96	9.7	10.9	1.70
5	In-BOX	2.4	25	2.6	7.9	1.30
6	SaBOX	4.0	>99	10.0	21.0	1.26
7	PMDETA	4.0	11.2	1.2	288.2	3.29
8	Me$_6$TREN	4.0	4.8	0.6	54.0	2.75
9	In-BOX	4.0	36	3.7	12.3	1.15
10	PMDETA	24.0	22.5	2.4	295.2	2.42
11	Me$_6$TREN	24.0	6.0	0.7	84.4	2.04
12	In-BOX	21.0	95	9.6	18.7	1.28

[a] Reaction conditions: n(MMA)/n(BPN)/n(CuBr$_2$)/n(ligand)/n(Cu(0)) = 100:1:0.5:1:2, DMSO used as the solvent (50% V_{total}), 25 °C. [b] Monomer conversion measured by ^{1}H NMR.

To understand the insight of the results, we conducted cyclic voltammetry (CV) of L/CuBr$_2$. Potentials were recorded versus the saturated calomel electrode using a 0.1 M Bu$_4$NPF$_6$ salt bridge. Figure 1 shows the CV data recorded for SaBOX/CuBr$_2$, which indicated good reversibility, as seen by their relatively small ΔE_p value. The $E_{1/2}$ [$E_{1/2} = (E_{p,a} + E_{p,c})/2$] for SaBOX/CuBr$_2$ was calculated as 0.216 V, which was much higher than those for PMDETA/CuBr$_2$ and Me$_6$TREN/CuBr$_2$ (−0.122 and −0.387 V, respectively). Correspondingly, the K_{ATRP} value for SaBOX/CuBr$_2$ was very low ($\leq 10^{-10}$), as estimated through correlation to the linear plot between the logarithm of K_{ATRP} and measured $E_{1/2}$ values by Matyjaszewski. Because complexes with lower measured $E_{1/2}$ are generally more active catalysts with higher K_{ATRP} for a wide range of Cu-based catalysts,[34−38] this result indicated that the SaBOX/CuBr$_2$ was much less active than the complexes with PMDETA and Me$_6$TREN as ligands. However, under the same conditions, the SaBOX/CuBr$_2$ complex performed much better in the supplemental activation and reducing agent (SARA) ATRP of MMA, as shown in Table 1 (run 1 vs runs 2−3). The reason is probably that the highly active catalysts could generate a large number of radicals at the early stages of polymerization that terminated before the system reaches equilibrium.[34−38] This conjecture was verified by the following experiments. First, as shown in Table 1, the monomer conversion changed very little by extending the reaction time from 2.4 to 4 h and even 24 h (runs 2−3, 7−8, and 10−11) in the polymerizations of MMA by employing the complexes bearing PMDETA or Me$_6$TREN. In contrast, SaBOX could afford a quantitative conversion and a narrow MWD ($Đ$ = 1.26) by prolonging the reaction time to 4 h (run 6). Furthermore, through in situ NMR experiments using DMSO-d_6 as the solvent, we observed that in the system of initiator BPN with catalyst [n(BPN)/n(CuBr$_2$)/n(ligand)/n(Cu(0)) = 2:1:2:4], PMEDTA/CuBr$_2$/Cu(0), or Me$_6$TREN/CuBr$_2$/Cu(0), the signals of BPN disappeared at the initial stage of reaction (within 0.5 h), indicating that C−Br of BPN completely dissociated shortly after being mixed with the catalyst. In comparison, under the same conditions, the signals of the initiator were clearly visible in the system of BPN with SaBOX/CuBr$_2$/Cu(0) (Figure 2). These findings suggested that our SaBOX/copper catalyst might lower the growing radical concentration and prolong the time scale of living polymerization of MMA and thus achieved much higher polymerization efficiency and much better controllability compared with catalytic systems utilizing PMDETA or Me$_6$TREN as the ligand.

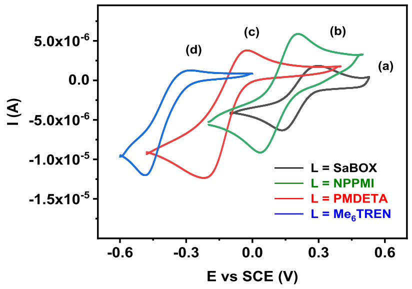


Figure 1. CV measurements of L/CuBr$_2$, $E_{1/2} = (E_{p,a} + E_{p,c})/2$. (a) SaBOX/CuBr$_2$: $E_{1/2}$ = 0.216 V; (b) NPPMI/CuBr$_2$: $E_{1/2}$ = 0.121 V; (c) PMDETA/CuBr$_2$: $E_{1/2}$ = −0.122 V; (d) Me$_6$TREN/CuBr$_2$: $E_{1/2}$ = −0.387 V.

The copper catalyst with N-(n-propyl)pyridylmethanimine (NPPMI) as the ligand, which has a similar Cu(I)/Cu(II) redox potential (i.e., K_{ATRP}) to the SaBOX/copper system (Figure 1),[34] was employed for the ATRP of MMA for comparison. As shown in Table 1 (run 4), at DP$_{target}$ = 100, this ligand achieved the polymerization controllability between

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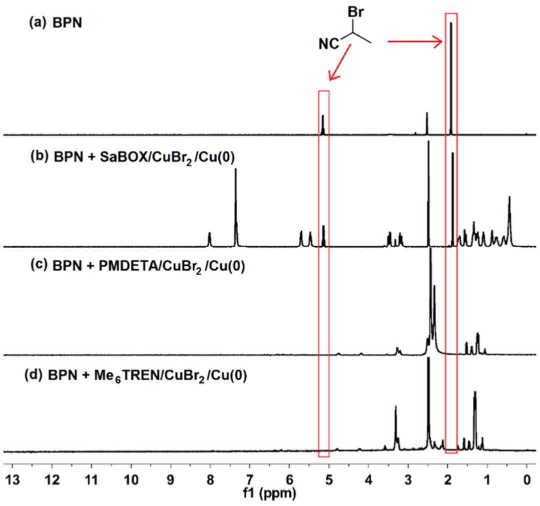

Figure 2. Overlay of ^{1}H NMR (DMSO-d_6 25 °C) spectra of (a) BPN; (b) BPN + SaBOX/CuBr$_2$/Cu(0); (c) BPN + PMDETA/CuBr$_2$/Cu(0); (d) BPN + Me$_6$TREN/CuBr$_2$/Cu(0). n(BPN)/n(CuBr$_2$)/n(ligand)/n(Cu(0)) = 2:1:2:4; Before the measurements, the initiator and catalyst were mixed for about half an hour.

those by SaBOX and PMDETA, giving a moderately broad $Đ$ of 1.70, indicating that the catalyst possessing a low K_{ATRP} was beneficial to obtain a well-controlled polymerization in the employed system. Besides, under the same conditions, we also conducted the polymerizations using indane bisoxazoline (In-BOX, Scheme 1) as the ligand, which obtained much lower MMA conversions than those by SaBOX, within the same time frame (run 1 vs run 5, run 6 vs run 9). This result demonstrated that the introduction of "side arms" into the In-BOX ligand was vital to achieve high polymerization efficiency.

SARA ATRP of MMA Targeting Different DPs. Subsequently, in order to probe the potential of the system with SaBOX in maintaining control over higher MWs, we conducted a range of polymerizations targeting polymerization degrees (DP$_{target}$) from 200 to 10 000. With the same dosage of the catalyst and initiator, when setting the initial concentration ratio of MMA and BPN as 200, the polymerization rate was still very fast; however, the MWD was greatly broadened to 1.68 (run 1 in Table 2). As is well known,[4] the solvent can dramatically affect the reaction rate and the polymerization control in ATRP, mainly because of the effect on the value of K_{ATRP}, the X−Cu(II)/L dissociation, and/or competitive complexation. In order to obtain fast and very controlled polymerization, we switched the solvent from DMSO to isopropanol (IPA) at DP$_{target}$ = 100, which resulted in a narrower MWD ($Đ$ = 1.15) but slower polymerization rate, giving 87% conversion in 10 h (run 2). To have advantage of both solvents, we next employed a mixed solvent of DMSO and IPA.

As shown in Table S2, with the increase of IPA/DMSO ratio (V/V) in the mixed solvent, the polymerization rate gradually slowed down, but the controllability was gradually improved (the measured value of MW was gradually close to the calculated one, and the MWD was gradually narrowed). For example, the polymerization of MMA in IPA/DMSO [7/1 (V/V)] achieved a fast polymerization reaching 90% conversion in 6.5 h with a narrow MWD ($Đ$ = 1.19, run 3 in Table 2). It was found that the polymerization of MMA proceeded with first-order kinetics with respect to the reaction time in the mixed solvent (IPA/DMSO = 7/1), which indicated the constant radical concentration and the very controlled process, as shown in Figure S1a (Table S3). Figure S1b showed the dependence of M_n and M_w/M_n on the monomer conversion for this polymerization. The experimental MWs matched the calculated ones, and the MWDs were narrow ($Đ$ = 1.18−1.40).

As shown in Table 2, the polymerization reaction with a DP$_{target}$ of 200 proceeded mildly in the mixed solvent (IPA/DMSO = 7/1), affording 78% conversion in 16 h and narrowly distributive MW ($Đ$ = 1.25). As the monomer conversion could not be improved by extending time, because the reaction mixture was difficult to stir in the later stage, we increased the proportion of DMSO to IPA/DMSO = 4/1 and improved the monomer conversion to 85%. Under the identical conditions, the polymerization reaction with the DP$_{target}$ of 400, afforded 81% conversion in 16.5 h and a $Đ$ of 1.55. A high conversion of 88% in 9 h, a high MW of 55.4 kg/mol, and a narrower MWD of 1.31 were achieved by increasing reaction temperature to 40 °C. Further increasing DP$_{target}$ to 1000, the polymerization reaction was still well controlled, producing poly(methyl methacrylate) (PMMA) with a high MW of 86.6 kg/mol

Table 2. SARA ATRP of MMA Targeting Different DPs[a]

run	DP$_{target}$	ligand	IPA/DMSO (V/V)	t (h)	conv.[b] (%)	$M_{n,theory}$ (kg/mol)	$M_{n,GPC}$ (kg/mol)	$Đ$
1	200	SaBOX	0/1	3.0	85	17.3	39.2	1.68
2	100	SaBOX	1/0	10.0	87	8.8	12.7	1.15
3	100	SaBOX	7/1	6.5	90	9.1	11.9	1.19
4	200	SaBOX	7/1	16.0	78	15.8	13.2	1.25
5	200	SaBOX	4/1	16.0	85	17.2	28.7	1.13
6	400	SaBOX	4/1	16.5	81	32.6	27.0	1.55
7	400	SaBOX	4/1	9.0	88	35.4	55.4	1.31
8	1000	SaBOX	4/1	22.0	68	68.2	86.6	1.13
9	5000	SaBOX	4/1	24.0	64	320.5	468.9	1.49
10	10 000	SaBOX	4/1	26.0	54	540.8	740.7	1.50
11	10 000	PMDETA	4/1	26.0	16	160.3	316.0	4.26
12	10 000	Me$_6$TREN	4/1	26.0	18	180.3	274.9	2.19
13	10 000	NPPMI	4/1	26.0	32	320.5	263.4	1.56
14	10 000	In-BOX	4/1	26.0	45	450.7	470.1	1.86

[a] Reaction conditions: n(MMA)/n(BPN)/n(CuBr$_2$)/n(ligand)/n(Cu(0)) = DP$_{target}$:1:0.5:1:2, IPA/DMSO was used as the solvent (50% V_{total}), 25 °C (runs 1−6) or 40 °C (runs 7−14). [b] Monomer conversion measured by ^{1}H NMR.

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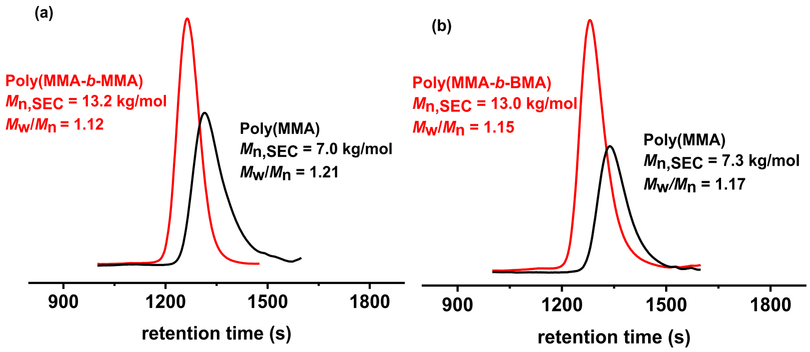


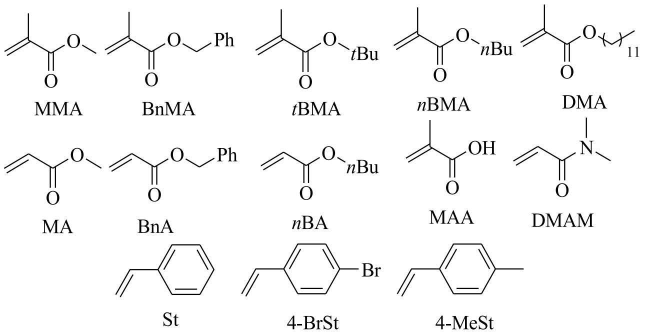
Figure 3. GPC traces of (a) in situ chain extension of PMMA and (b) in situ block copolymer PMMA-*b*-PBMA.

and a very narrow MWD of 1.13. Next, we continued to increase the DP_{target} to 5000 and 10 000 (runs 9−10) with copper loading of 100 and 50 ppm, which achieved ultrahigh MWs of 469 and 741 kg/mol and an acceptable MWD of about 1.5 (Figure S2), respectively. These results were very remarkable, as much lower conversion and much poorer controllability were observed when PMDETA and Me_6TREN were employed as the ligands under the same conditions (runs 11−12). Besides, the result by NPPMI was also inferior to that by SaBOX, in terms of polymerization efficiency and controllability (run 13). These results further suggested that our SaBOX/copper catalytic system showed unprecedentedly high efficiency in ATRP of MMA under current conditions. The In-BOX ligand was also proved less efficient than the SaBOX ligand in terms of monomer conversion and control over MW, further suggesting that the introduction of "side arms" was beneficial to improve the polymerization efficiency and controllability (run 14).

In Situ Chain Extension Experiments. In order to assess the end group fidelity of the system, the isolated PMMA produced in the mixed solvent [IPA/DMSO ratio (V/V) = 7/1] was analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, which revealed very high end group fidelity with the major polymer peak distribution corresponding to bromine-terminated PMMA (Figure S3). Besides, in situ chain extensions of PMMA with a second aliquot of MMA were conducted furnishing a higher MW polymer (M_n = 13.2 kg/mol) without increase in the initial dispersity of the macroinitiator, with the conversions of >99 and 75%, respectively, for the first and second block (Figure 3a and Table S4). Importantly, very little tailing in the low MW region was observed for the polymer with higher MW, suggesting an efficient reinitiation of PMMA and high end group fidelity under the selected conditions. *n*-Butyl methacrylate (*n*BMA) was also employed to in situ chain extension of a PMMA macroinitiator, yielding a well-defined *p*(MMA)-*b*-*p*(*n*BMA) diblock copolymer with a final dispersity of 1.15 and a final M_n of 13.0 kg/mol (Figure 3b and Table S5). Again, it should be noted that the conversion of the second block was pushed to 86%, yielding even lower MWD than that of the PMMA macroinitiator. Overall, these results demonstrated that the combination of BPN, IPA/DMSO, SaBOX/$CuBr_2$, and Cu(0) powder could successfully mediate the fast and controlled polymerization of MMA, yielding low dispersed polymers even at very high conversions and leading to the in situ synthesis of well-defined diblock copolymers.

SARA ATRP of Different Monomers Employing SaBOX. The polymerizations of different monomer families were investigated to evaluate the range of application and robustness of this new ATRP system. The results summarized in Table 3 showed that the system was very versatile and robust, as it was successfully employed for the controlled polymerization of various methacrylic monomers [*n*-butyl (*n*BMA), dodecyl (DMA), and benzyl methacrylates (BnMA)] at room temperature. All the polymerizations proceeded relatively fast (furnishing 85% to quantitative conversions overnight), and the resultant polymers possessed MWs close to theoretical values and relatively narrow MWDs (Đ = 1.26−1.43). By extending the reaction time to 32 h, we also got a high conversion (87%) and a controlled polymerization of *tert*-

Table 3. SARA ATRP of Different Monomers[a]



run	monom.	*t* (h)	conv.[b] (%)	$M_{n,theory}$ (kg/mol)	$M_{n,GPC}$ (kg/mol)	Đ
1	BnMA	16	85	15.1	11.9	1.43
2	*t*BMA	32	87	12.5	11.7	1.37
3	*n*BMA	12	88	12.6	14.2	1.33
4	MA	10	86	7.5	13.5	1.26
5[c]	DMA	13	>99	12.7	18.6	1.43
6[c]	BnA	14	84	7.0	11.7	1.47
7[c]	*n*BA	11	91	6.0	10.5	1.39
8[d]	St	48	41	2.3	5.1	1.45
9[e]	St	24	71	3.8	2.5	1.25
10[f]	4-BrSt	32	68	6.4	6.4	1.39
11[e]	4-MeSt	48	61	3.7	3.0	1.37
12[g]	MAA	13	58	5.1	20.6	1.16
13[c]	DMAM	1	84	4.3	13.5	1.65

[a] Reaction conditions: $n(M)/n(\text{initiator})/n(CuBr_2)/n(\text{ligand})/n(Cu(0)) = DP_{target}:1:0.5:1:2$, DP_{target} = 100, IPA/DMSO [7/1 (V/V)] was used as the solvent (50% V_{total}), at 25 °C. [b] Monomer conversion measured by ^1H NMR. [c] Variation: DP_{target} = 50. [d] Variation: DP_{target} = 50, without solvent. [e] Variation: DP_{target} = 50, at 60 °C, without solvent. [f] Variation: DP_{target} = 50, at 40 °C, without solvent. [g] Variation: IPA/DMSO = 0/1 (V/V).

butyl methacrylate (*t*BMA). Typically, active ligands provide good control in polymerizing high k_p monomers (e.g., acrylates and acrylamides), and less active ligands achieve better control in the polymerization of low k_p monomers (e.g., methacrylates).[39,40] Remarkably, we achieved a very controlled polymerization of methyl acrylate (MA), reaching a high conversion of 86%, indicating that our SaBOX ligand was able to provide good control in polymerizing both high and low k_p monomers. Hawker's group has recently reported a universal system, by which no polymer was detected in 40 h for the polymerization of styrene at room temperature.[22] Unexpectedly, our system facilitated a controlled polymerization of styrene at 25 °C, although the polymerization proceeded mildly, giving a conversion of 41% in 48 h. By gradually increasing the temperature from room temperature to 60 °C, we obtained well-defined poly(styrene) exhibiting a narrow MWD ($Đ$ = 1.25) at 71% conversion. Several other acrylate- and styrene-type monomers, including *n*-butyl acrylate (*n*BA), benzyl acrylate (BnA), 4-bromostyrene (4-BrSt), and 4-methylphenylene (4-MeSt), have also been submitted to these conditions. As shown in the table, we got controlled polymerizations with high conversions of 84% in 14 h and 91% in 11 h for the polymerizations of BnA and *n*BA, respectively (runs 6−7). The polymerizations of 4-BrSt and 4-MeSt were both controlled and achieved conversions of 68 and 61%, at 40 and 60 °C, respectively (runs 10−11). The polymerizations of functional monomers were also conducted to explore the versatility and robustness of the system. The polymerization of *N*,*N*-dimethylacrylamide (DMAM) afforded a high conversion of 84% in 1 h. In addition, a conversion of 58% in 13 h and a narrow MWD ($Đ$ = 1.16) were obtained using our catalytic system in the polymerization of methacrylic acid (MAA), which is very difficult to polymerize and seldom polymerized via ATRP, although the experimental MW value was four times the theoretical one.[41]

Determinations of the Equilibrium Constant and Activation Rate Constant. The K_{ATRP} measurement of the SaBOX/CuBr system was conducted using the same method in Matyjaszewski's work.[38] Ultraviolet−visible (UV−vis) spectrometric experiments were used to follow the evolution of Cu(II) species. From the graph for the determination of K_{ATRP} [Figure S4d, $F(Y)$ vs t] via the modified Fischer's equation (eq S1), we calculated the K_{ATRP} value. In acetonitrile and at 25 °C, we employed EBiB as the initiator and found a low K_{ATRP} value of 5.9×10^{-11}, which is lower than most of the catalytic systems reported by Matyjaszewski[38] and is consistent with the estimation on the basis of the correlation with the redox potential. The activation rate constant (k_{act}) was also measured for the SaBOX/CuBr catalyst based on the method in Matyjaszewski's work,[42,43] by using gas chromatography to monitor the consumption of the initiator (EBiB). The radicals originating from homolytic halogen abstraction from the alkyl halides are irreversibly trapped by a stable nitroxide radical, 2,2,6,6-tetramethylpiperidinyl-1-oxy, to yield the corresponding alkoxyamines. Trichlorobenzene was used as the internal standard. Based on eq S2, the k_a value was determined from the slope of the pseudo-first-order plot (Figure S5). We obtained a low k_{act} value of 9.5×10^{-4} $M^{-1} \cdot s^{-1}$, and thus, the deactivation rate constant (k_{deact}) value was extrapolated as 1.6×10^7 $M^{-1} \cdot s^{-1}$ ($k_{deact} = k_{act}/K_{ATRP}$). Compared with those catalytic systems reported in literature studies,[34] our SaBOX/copper catalytic system contains very slow activating Cu(I) species and relatively fast deactivating Cu(II) species. Therefore, the SaBOX/copper catalyst could lower the growing radical concentration and prolong the time scale of living polymerization and thus realized high polymerization efficiency.

Notably, the evolutions of Cu(II) species were also monitored by the UV−vis spectrometric experiments with BPN as the initiator (in acetonitrile and at 25 °C; $[CuBr]_0 = [Ligand]_0 = [BPN]_0 = 5$ mM), employing SaBOX and PMDETA as the ligands. As shown in Figure S6, after the reaction for 12 000 s, the concentration of PMDETA/Cu(II) species was 1.85 mM [with a Cu(I) conversion of 37%], while the concentration of SaBOX/Cu(II) species was only 0.14 mM [with a Cu(I) conversion of 3%]. As the accumulation of Cu(II) species is positively correlated with the extent of radical−radical terminations,[34−38] it suggests that the extent of radical−radical terminations in the SaBOX/copper system was much lower than that in the PMDETA/copper system, which may be the reason why our copper/SaBOX system has good controllability, and the resultant polymers possess high end group fidelity.

■ CONCLUSIONS

In conclusion, a new highly efficacious SARA ATRP system using SaBOX as the ligand was reported for the controlled polymerization of various methacrylates, acrylates, styrenes, DMAM, and MAA near room temperature. The polymerizations of MMA were very rapid and could furnish ultrahigh MW polymers (up to 741 kg/mol) with narrow MWDs ($Đ$ = 1.13−1.50) under common conditions. The excellent controllability of the polymerizations and the high end group fidelity of the resultant polymers were confirmed by the successful synthesis of well-defined block polymers via in situ chain extension after the quantitative conversion of the first block. Thus, the employment of the catalytic system possessing relatively low K_{ATRP} might lower the growing radical concentration and prolong the time scale of living polymerization and then realize the simultaneous achievement of excellent controllability, high efficiency, and high MW. Besides, the introduction of "side arms" into the In-BOX ligand was vital to achieve high polymerization efficiency and controllability. This paves a way for the development of catalysts for highly efficient ATRP.

■ EXPERIMENTAL SECTION

General ATRP Procedure. All polymerizations were set up and performed under an atmosphere of oxygen-free, dry argon using standard Schlenk-line techniques or inside a nitrogen-filled glovebox. In an ampule equipped with a magnetic stirrer bar, a mixture of $CuBr_2$, ligand, and Cu(0) powder in the solvent was stirred at room temperature for 2 h under the atmosphere of nitrogen. After that, the monomer and initiator were added into the ampule. The ampules were placed at a certain temperature. After stirring for the allotted period of time, an aliquot (0.05 mL) was removed and quenched with deuterated chloroform ($CDCl_3$) (0.5 mL). Conversion was determined by integration of the monomer versus polymer resonances in the ^1H NMR spectrum of the crude product. After completion of the reaction, the contents of the ampules were dissolved in tetrahydrofuran (THF). The solution was filtered through a glass funnel with neutral alumina. The filtrate was concentrated under reduced pressure. The residuals were resolved with 5 mL of THF. This solution was added to an approximately 50-fold excess of rapidly stirred methanol. The precipitate that formed was filtered and washed with methanol. The precipitate was dried to constant weight in a vacuum oven at 50 °C.

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■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b01797.

> Supplementary SARA ATRP of MMA; first-order kinetic study and evolution of MW and Đ; first-order kinetic plot; GPC traces, MALDI-TOF mass spectrum; in situ chain extension experiments; details on the determinations of equilibrium constant and activation rate constant (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *101*, 2921−2990.

(2) Kamigaito, M.; Ando, T.; Sawamoto, M. Metal-Catalyzed Living Radical Polymerization. *Chem. Rev.* **2001**, *101*, 3689−3746.

(3) Tsarevsky, N. V.; Matyjaszewski, K. "Green" Atom Transfer Radical Polymerization: From Process Design to Preparation of Well-Defined Environmentally Friendly Polymeric Materials. *Chem. Rev.* **2007**, *107*, 2270−2299.

(4) Matyjaszewski, K.; Tsarevsky, N. V. Macromolecular Engineering by Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* **2014**, *136*, 6513−6533.

(5) Wang, R.; Luo, Y.; Li, B.-G.; Zhu, S. Modeling of Branching and Gelation in RAFT Copolymerization of Vinyl/Divinyl Systems. *Macromolecules* **2009**, *42*, 85−94.

(6) Xue, Z.; Linh, N. T. B.; Noh, S. K.; Lyoo, W. S. Phosphorus-Containing Ligands for Iron(III)-Catalyzed Atom Transfer Radical Polymerization. *Angew. Chem., Int. Ed.* **2008**, *47*, 6426−6429.

(7) Bai, L.; Zhang, L.; Cheng, Z.; Zhu, X. Activators generated by electron transfer for atom transfer radical polymerization: recent advances in catalyst and polymer chemistry. *Polym. Chem.* **2012**, *3*, 2685−2697.

(8) Hu, R.; Leung, N. L. C.; Tang, B. Z. AIE macromolecules: syntheses, structures and functionalities. *Chem. Soc. Rev.* **2014**, *43*, 4494−4562.

(9) Li, B.; Yu, B.; Ye, Q.; Zhou, F. Tapping the Potential of Polymer Brushes through Synthesis. *Acc. Chem. Res.* **2015**, *48*, 229−237.

(10) Bian, C.; Zhou, Y.-N.; Guo, J.-K.; Luo, Z.-H. Photoinduced Fe-mediated atom transfer radical polymerization in aqueous media. *Polym. Chem.* **2017**, *8*, 7360−7368.

(11) Braunecker, W. A.; Matyjaszewski, K. Controlled/living radical polymerization: Features, developments, and perspectives. *Prog. Polym. Sci.* **2007**, *32*, 93−146.

(12) Matyjaszewski, K. Macromolecular engineering: From rational design through precise macromolecular synthesis and processing to targeted macroscopic material properties. *Prog. Polym. Sci.* **2005**, *30*, 858−875.

(13) Barner-Kowollik, C.; Buback, M.; Egorov, M.; Fukuda, T.; Goto, A.; Olaj, O. F.; Russell, G. T.; Vana, P.; Yamada, B.; Zetterlund, P. B. Critically evaluated termination rate coefficients for free-radical polymerization: Experimental methods. *Prog. Polym. Sci.* **2005**, *30*, 605−643.

(14) Kwiatkowski, P.; Jurczak, J.; Pietrasik, J.; Jakubowski, W.; Mueller, L.; Matyjaszewski, K. High Molecular Weight Polymethacrylates by AGET ATRP under High Pressure. *Macromolecules* **2008**, *41*, 1067−1069.

(15) Mapas, J. K. D.; Thomay, T.; Cartwright, A. N.; Ilavsky, J.; Rzayev, J. Ultrahigh Molecular Weight Linear Block Copolymers: Rapid Access by Reversible-Deactivation Radical Polymerization and Self-Assembly into Large Domain Nanostructures. *Macromolecules* **2016**, *49*, 3733−3738.

(16) Arita, T.; Kayama, Y.; Ohno, K.; Tsujii, Y.; Fukuda, T. High-pressure atom transfer radical polymerization of methyl methacrylate for well-defined ultrahigh molecular-weight polymers. *Polymer* **2008**, *49*, 2426−2429.

(17) Pietrasik, J.; Hui, C. M.; Chaladaj, W.; Dong, H.; Choi, J.; Jurczak, J.; Bockstaller, M. R.; Matyjaszewski, K. Silica-Polymethacrylate Hybrid Particles Synthesized Using High-Pressure Atom Transfer Radical Polymerization. *Macromol. Rapid Commun.* **2011**, *32*, 295−301.

(18) Nicolaÿ, R.; Kwak, Y.; Matyjaszewski, K. A Green Route to Well-Defined High-Molecular-Weight (Co)polymers Using ARGET ATRP with Alkyl Pseudohalides and Copper Catalysis. *Angew. Chem., Int. Ed.* **2010**, *49*, 541−544.

(19) Percec, V.; Guliashvili, T.; Ladislaw, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. Ultrafast Synthesis of Ultrahigh Molar Mass Polymers by Metal-Catalyzed Living Radical Polymerization of Acrylates, Methacrylates, and Vinyl Chloride Mediated by SET at 25 °C. *J. Am. Chem. Soc.* **2006**, *128*, 14156−14165.

(20) Mao, B. W.; Gan, L. H.; Gan, Y. Y. Ultra high molar mass poly[2-(dimethylamino)ethyl methacrylate] via atom transfer radical polymerization. *Polymer* **2006**, *47*, 3017−3020.

(21) Nguyen, N. H.; Leng, X.; Percec, V. Synthesis of ultrahigh molar mass poly(2-hydroxyethyl methacrylate) by single-electron transfer living radical polymerization. *Polym. Chem.* **2013**, *4*, 2760−2766.

(22) Whitfield, R.; Anastasaki, A.; Nikolaou, V.; Jones, G. R.; Engelis, N. G.; Discekici, E. H.; Fleischmann, C.; Willenbacher, J.; Hawker, C. J.; Haddleton, D. M. Universal Conditions for the Controlled Polymerization of Acrylates, Methacrylates, and Styrene via Cu(0)-RDRP. *J. Am. Chem. Soc.* **2017**, *139*, 1003−1010.

(23) Ren, J. M.; McKenzie, T. G.; Fu, Q.; Wong, E. H. H.; Xu, J.; An, Z.; Shanmugam, S.; Davis, T. P.; Boyer, C.; Qiao, G. G. Star Polymers. *Chem. Rev.* **2016**, *116*, 6743−6836.

(24) Mendonça, P. V.; Ribeiro, J. P. M.; Abreu, C. M. R.; Guliashvili, T.; Serra, A. C.; Coelho, J. F. J. Thiourea Dioxide as a Green and Affordable Reducing Agent for the ARGET ATRP of Acrylates, Methacrylates, Styrene, Acrylonitrile, and Vinyl Chloride. *ACS Macro Lett.* **2019**, *8*, 315−319.

(25) Zhou, J.; Tang, Y. The development and application of chiral trisoxazolines in asymmetric catalysis and molecular recognition. *Chem. Soc. Rev.* **2005**, *34*, 664−676.

(26) Liao, S.; Sun, X.-L.; Tang, Y. Side Arm Strategy for Catalyst Design: Modifying Bisoxazolines for Remote Control of Enantioselection and Related. *Acc. Chem. Res.* **2014**, *47*, 2260−2272.

(27) Ferro, R.; Milione, S.; Bertolasi, V.; Capacchione, C.; Grassi, A. Iron Complexes of Bis(oxazoline) Ligand as Novel Catalysts for Efficient Atom Transfer Radical Polymerization of Styrene. *Macromolecules* **2007**, *40*, 8544−8546.

(28) Schaubach, S.; Wang, X.-Y.; Li, J.-F.; Sun, X.-L.; Wang, S. R.; Tang, Y. Yb(NTf_2)$_3$/HFIP induced high isotacticity in atom transfer

radical polymerization of methyl methacrylate. *Polym. Chem.* **2018**, *9*, 4711−4715.

(29) Wang, X.-Y.; Sun, X.-L.; Chen, Z.-H.; Wang, F.; Wang, S. R.; Tang, Y. Highly efficient access to well-defined linear polymers with substantial vinyl pendants via ATRP of divinyl monomers. *Polym. Chem.* **2018**, *9*, 4309−4315.

(30) Wang, X.-Y.; Sun, X.-L.; Wang, F.; Tang, Y. SaBOX/Copper Catalysts for Highly Syndio-Specific Atom Transfer Radical Polymerization of Methyl Methacrylate. *ACS Catal.* **2017**, *7*, 4692−4696.

(31) Wang, X.-Y.; Chen, Z.-H.; Sun, X.-L.; Tang, Y. Low Temperature Effect on ATRP of Styrene and Substituted Styrenes Enabled by SaBOX Ligand. *Polymer* **2019**, *178*, 121630.

(32) Anastasaki, A.; Waldron, C.; Wilson, P.; McHale, R.; Haddleton, D. M. The importance of ligand reactions in Cu(0)-mediated living radical polymerisation of acrylates. *Polym. Chem.* **2013**, *4*, 2672−2675.

(33) Anastasaki, A.; Waldron, C.; Wilson, P.; Boyer, C.; Zetterlund, P. B.; Whittaker, M. R.; Haddleton, D. High Molecular Weight Block Copolymers by Sequential Monomer Addition via Cu(0)-Mediated Living Radical Polymerization (SET-LRP): An Optimized Approach. *ACS Macro Lett.* **2013**, *2*, 896−900.

(34) Tang, W.; Kwak, Y.; Braunecker, W.; Tsarevsky, N. V.; Coote, M. L.; Matyjaszewski, K. Understanding Atom Transfer Radical Polymerization: Effect of Ligand and Initiator Structures on the Equilibrium Constants. *J. Am. Chem. Soc.* **2008**, *130*, 10702−10713.

(35) O'Reilly, R. K.; Gibson, V. C.; White, A. J. P.; Williams, D. J. Design of Highly Active Iron-Based Catalysts for Atom Transfer Radical Polymerization: Tridentate Salicylaldiminato Ligands Affording near Ideal Nernstian Behavior. *J. Am. Chem. Soc.* **2003**, *125*, 8450−8451.

(36) Ando, T.; Kamigaito, M.; Sawamoto, M. Catalytic Activities of Ruthenium(II) Complexes in Transition-Metal-Mediated Living Radical Polymerization: Polymerization, Model Reaction, and Cyclic Voltammetry. *Macromolecules* **2000**, *33*, 5825−5829.

(37) Tsarevsky, N. V.; Braunecker, W. A.; Brooks, S. J.; Matyjaszewski, K. Rational Selection of Initiating/Catalytic Systems for the Copper-Mediated Atom Transfer Radical Polymerization of Basic Monomers in Protic Media: ATRP of 4-Vinylpyridine. *Macromolecules* **2006**, *39*, 6817−6824.

(38) Tang, W.; Tsarevsky, N. V.; Matyjaszewski, K. Determination of Equilibrium Constants for Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* **2006**, *128*, 1598−1604.

(39) Matyjaszewski, K. Atom Transfer Radical Polymerization (ATRP): Current Status and Future Perspectives. *Macromolecules* **2012**, *45*, 4015−4039.

(40) Nanda, A. K.; Matyjaszewski, K. Effect of [PMDETA]/[Cu(I)] Ratio, Monomer, Solvent, Counterion, Ligand, and Alkyl Bromide on the Activation Rate Constants in Atom Transfer Radical Polymerization. *Macromolecules* **2003**, *36*, 1487−1493.

(41) Fantin, M.; Isse, A. A.; Venzo, A.; Gennaro, A.; Matyjaszewski, K. Atom Transfer Radical Polymerization of Methacrylic Acid: A Won Challenge. *J. Am. Chem. Soc.* **2016**, *138*, 7216−7219.

(42) Matyjaszewski, K.; Göbelt, B.; Paik, H.-j.; Horwitz, C. P. Tridentate Nitrogen-Based Ligands in Cu-Based ATRP: A Structure-Activity Study. *Macromolecules* **2001**, *34*, 430−440.

(43) Tang, W.; Nanda, A. K.; Matyjaszewski, K. Effect of [Pyridylmethanimine]/[Cu^I] Ratio, Ligand, Solvent and Temperature on the Activation Rate Constants in Atom Transfer Radical Polymerization. *Macromol. Chem. Phys.* **2005**, *206*, 1171−1177.

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