

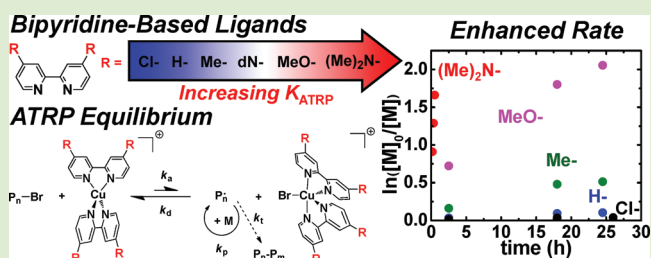
Highly Active Bipyridine-Based Ligands for Atom Transfer Radical Polymerization

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S Supporting Information

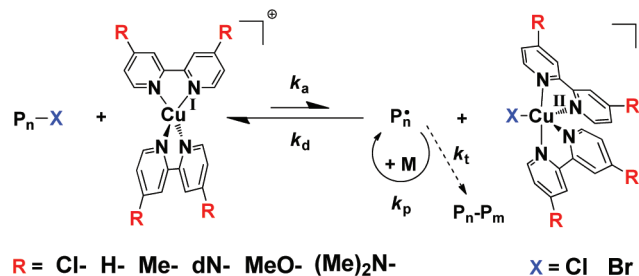
ABSTRACT: A series of 2,2'-bipyridines with 4,4'-substituents (R-bpy) were investigated for atom transfer radical polymerization (ATRP) of methyl acrylate (MA) and methyl methacrylate (MMA). Ligand substituents with a large range of Hammett parameters (R = Cl, H, Me, dinonyl (dN), MeO, and (Me)₂N) were studied with cyclic voltammetry (CV), revealing that increasing the strength of electron donating groups (EDGs) resulted in more stable Cu^{II} complexes and larger ATRP equilibrium constants. Normal ATRP experiments confirmed the obtained CV data by showing the fastest rates of polymerization with R-bpy ligands containing EDGs ((Me)₂N and MeO) and the slowest with electron withdrawing Cl. A 400-fold increase in the polymerization rate was observed with bpy ligands containing *p*-(Me)₂N compared to H substituents. Linear increases in molecular weight with monomer conversion, and narrow molecular weight distributions were obtained with (Me)₂N-bpy and MeO-bpy ligands. Low catalyst concentrations of 50 to 100 parts-per-million (ppm) were successfully employed with highly active R-bpy ligands (R = MeO and (Me)₂N) and found to be effective in polymerizing MA and MMA, respectively, with narrow molecular weight distributions <1.3.



ATRP is one of the most powerful controlled/living radical polymerization (CRP) techniques available to synthesize well-defined macromolecules under versatile experimental conditions.^{1–4} With such a technique, the synthetic polymer chemist may precisely design macromolecular architectures using a toolbox full of functionalities, compositions, and topologies with predetermined molecular weights (M_n) and narrow molecular weight distributions (M_w/M_n).^{5,6} Utility of ATRP encompasses a vast library of functional monomers from parent (meth)acrylates to styrenics and acrylamides, solvents (i.e., aqueous to organic), macromolecular architectures (e.g., stars and brushes), and reaction media (e.g., dispersions, emulsions, and homogeneous systems).^{7–11} To date, ATRP has witnessed significant advancements through processes including activators regenerated by electron transfer (ARGET),^{12,13} initiators for continuous activator regeneration (ICAR),¹² electrochemically mediated ATRP (eATRP),^{14,15} and variations thereof,^{16–18} which adhere to the criteria of CRP and require only ppm concentrations of catalyst. Despite these successes, great potential still exists to further improve the efficiency and versatility of ATRP through optimization and development of novel catalysts.¹⁹

ATRP is dictated by a dynamic reversible equilibrium (K_{ATRP} , Scheme 1) between dormant alkyl halides ($P_n\text{-Br}$) and lower oxidation state transition metal complexes ($\text{Cu}^{\text{I}}/\text{L}$, L = ligand), and the respective propagating radicals (P_n^\bullet) and higher oxidation state transition metal complexes ($\text{X-Cu}^{\text{II}}/\text{L}$). K_{ATRP} values, defined as the ratio of activation (k_a) and deactivation (k_d) rate constants, favor the dormant state ensuring concurrent growth of each polymer chain and minimizing the $[P_n^\bullet]$. In this

Scheme 1. Dormant-Active Equilibrium in ATRP



equilibrium, P_n^\bullet can propagate with monomer (k_p), be deactivated with $\text{X-Cu}^{\text{II}}/\text{L}$, or terminate (k_t) with other radicals, with a rate proportional to the corresponding rate constant. The ATRP equilibrium is also strongly dependent on four main variables: temperature,²⁰ pressure,²¹ solvent,²² and alkyl halide/catalyst.²³ Of these four variables, the strongest influence resides with the polymerization solvent and catalyst, spanning values over a range of 1×10^8 in both cases. Catalysts, however, provide synthetic freedom in ligand design to manipulate and tune catalytic properties, which have yet to be truly exploited in ATRP. At present, some of the most commonly employed and effective ligands in ATRP remain to be tris(2-(dimethylamino)ethyl)amine (Me_6TREN)²⁴ and tris(2-pyridylmethyl)amine

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(TPMA),²⁵ which are 1000× more active than the originally used 2,2'-bipyridine.^{26,27}

A variety of strategies exist to manipulate catalytic activity and properties through ligand design. For example, altered catalytic activity with so-called “pincer” type ligands has been shown to be effective by changing the steric bulk adjacent to the donor atoms in organonickel(II) complexes.^{28,29} In a similar system, catalyst complex activity could also be tuned electronically via electron donating/withdrawing substituents on the ligand.³⁰ 2,2'-Bipyridine (bpy) type ligands, the first successfully employed in Cu-mediated ATRP,^{26,27,31,32} can be modified with an array of functionalities providing a plethora of unique properties for asymmetric catalysis,³³ luminescence, and pH sensitivity,³⁴ and enhanced photocatalytic activity.³⁵ However, despite the vast array of modifications available, limited examples²³ of systematically changed structure–activity relationships exist in regard to ATRP ligand substituents using Hammett parameters. Fundamental investigations of this kind will provide the necessary knowledge to intelligently design active catalytic systems capable of further diminishing catalyst concentrations, expanding the range of accessible monomers, and producing well-defined polymers.

When considering electronic effects^{30,35} and general ATRP catalysts,^{23,36} it was anticipated that 4,4'-substituted 2,2'-bipyridine ligands could influence copper complex activity and the ATRP process. So far, reactivity of Cu-catalysts with *N*-based ligands have been correlated with the number of *N*-atoms (4 > 3 > 2), nature of *N*-atoms (alkyl amine ≈ pyridine > imine > aromatic amine), distance between *N*-atoms ($C_2 > C_3 > C_4$), and ligand topology (branched > cyclic > linear).³⁷ This work, however, is focused on examining the importance of electronic effects when employing various *para* substituents (R) in relatively less active bpy ligands, as shown in Scheme 1 and Table 1. These substituents range from electron withdrawing

Table 1. CV of 4,4'-Substituted 2,2'-Bipyridine Ligands

entry	R	σ_p^b	$E_{1/2}$ (V) ^a	ΔE_p (mV)
1	Cl	0.23	0.270	130
2	H	0.00	0.055	110
3	Me	−0.17	−0.048	125
4	dN	n/a	−0.055	120
5	MeO	−0.27	−0.088	105
6	(Me) ₂ N	−0.83	−0.313	145

^aV vs saturated calomel electrode (SCE) in MeCN and using conditions previously reported.²³ ^bAs reported in literature.⁴²

groups (EWGs: Cl) to electron donating groups (EDGs: Me, dN, MeO, (Me)₂N), representing the first systematic study to correlate structure–activity of substituents bearing variable Hammett parameters (σ_p : 0.23 to −0.83) to $E_{1/2}$ (K_{ATRP}) and to the polymerization rate. With these substituted-bpy ligands, we observed considerable enhancement of ATRP by employing EDGs in the polymerizations of acrylates. Strongly donating R-bpy ligands resulted in significant rate enhancements and controlled polymerizations utilizing ppm catalyst loadings; typically inaccessible to H-bpy and dN-bpy ligands.¹² All R-bpy ligands used in this work are commercially available except for (Me)₂N-bpy, which was prepared according to literature,³⁸ as outlined in the Supporting Information. X-Cu^{II}/R-bpy complexes should maintain a trigonal bipyramidal geometry, commonly observed for copper(II) bpy systems,^{37,39,40} independent of the 4,4'-substituents. This assumption was

based upon ruthenium based complexes with similar ligands, which maintained their octahedral geometry, Ru–N bond lengths, and N–Ru–N chelating angle regardless of the bpy substituent.³⁵

Prior to conducting ATRP, characterization of each complex was carried out using CV and the results are summarized in Table 1. CV provides a convenient tool to gain insight into the relative activities of copper complexes in ATRP through the correlation which exists between half-wave potentials ($E_{1/2}$) and ATRP equilibrium constants (K_{ATRP}).^{22,23} As evidenced in Table 1, moving to increasingly more electron donating *p*-substituents (i.e., R(EDG) = Cl < H < CH₃ < MeO < (Me)₂N) and more negative σ_p , leads to progressively more negative $E_{1/2}$ values. More negative $E_{1/2}$ values correspond to more stable Cu^{II}/L complexes and, therefore, result in larger K_{ATRP} values. Simply changing the 4,4'-substituent on the pyridine moiety from a hydrogen atom to a donating (Me)₂N functional group produced a 370 mV shift in the $E_{1/2}$ value, equivalent to a 10⁶ increase in K_{ATRP} .²² This $E_{1/2}$ value for (Me)₂N-bpy is similar to one of the most active complexes in ATRP with Me₆TREN. Similar substituent effects on redox properties were found with “pincer” type ligands³⁰ and ruthenium bpy complexes.³⁵ CV experiments also revealed larger than Nernstian value peak-to-peak separations (ΔE_p), which have been observed for Cu/R-bpy complexes in the past.^{23,41} Relatively large ΔE_p values correspond to slow reorganization of copper(I/II) redox states with specific coordination geometries.⁴¹

After characterization of each complex, scouting experiments were conducted to find a suitable polymerization solvent for comparison, providing a homogeneous reaction mixture for all catalysts. Polymerizations performed in MeCN were found to be largely heterogeneous for both MeO-bpy and (Me)₂N-bpy systems producing significant amounts of precipitated catalyst. The results of these polymerizations can be found in the Supporting Information (Figures S1–S2). However, in DMSO, homogeneous reaction mixtures were observed and enhanced polymerization rates resulted as consistent with known solvent effects on K_{ATRP} (Figure 1).²² The DMSO system will serve as the focus of our remaining discussion.

The CV results indicated that EDGs *para* to the *N*-donor atom would enhance catalytic activity in ATRP. To test this hypothesis a series of polymerizations were conducted under traditional ATRP conditions varying only the R-bpy ligand. During each polymerization monomer conversion, number average molecular weight (M_n), and the molecular weight distribution (M_w/M_n) were monitored as the polymerization progressed (Figure 1A,B). The fastest polymerization was observed with the most electron donating substituent (i.e., (Me)₂N), followed by MeO and dN, and the slowest with H and Cl substituents (Figure 1A). Nearly a 400× and 100× rate enhancement was observed from H-bpy to (Me)₂N-bpy and MeO-bpy ligands, respectively. This is smaller than anticipated for very large K_{ATRP} values expected from CV, due to radical termination and persistent radical effect.⁴³ Monomer conversions >80% were accomplished in about 0.5 h and 17 h with (Me)₂N-bpy and MeO-bpy, respectively, whereas the traditional H-bpy/dNbpy ligands required nearly a day to reach only about 40% conversion. Similar structure–reactivity behavior was observed with Ru/R-bpy complexes where EDGs (R = (Me)₂N, MeO) provided enhanced rates compared to alkyl groups (R = Me, *t*-butyl) during the photocatalytic oligomerization of α -methylstyrene.³⁵ Furthermore, EDG R-bpy ligands provided characteristics of a well-controlled

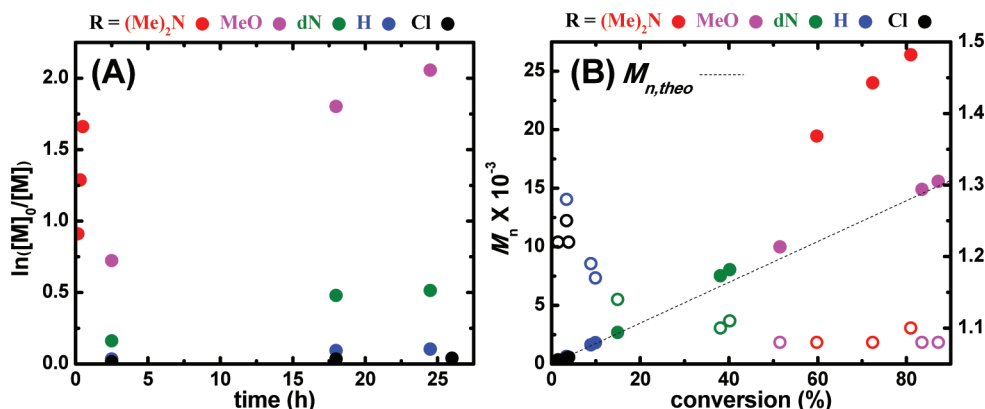


Figure 1. (A) First-order kinetics and (B) M_n and M_w/M_n vs conversion plots for various R-bpy ligands. Polymerizations were conducted with 5.55 M MA in 50 (v/v) % DMSO at 60 °C using the following molar ratios of $[MA]/[EBiB]/[R-bpy]/[CuBr]/[CuBr_2] = 200:1:2:0.9:0.1$.

Table 2. ATRP of MA and MMA with ppm Levels of Cu/R-bpy Ligands

entry	monomer	$[Cu^{II}Br_2]$ (ppm/equiv (X))	[R-bpy] (R/equiv (Y))	time (h)	conv. (%)	$M_{n,theo}$	$M_{n,GPC}$	M_w/M_n
1 ^a	MA	500/0.1	dN/0.20	2.0	24	4115	11200	1.98
				7.0	62	10692	16500	1.76
2 ^a	MA	500/0.1	MeO/0.20	2.0	35	6026	8930	2.39
				5.0	74	12706	16800	1.64
3 ^a	MA	500/0.1	(Me) ₂ N/0.20	1.0	54	9332	11300	1.17
				2.0	78	13464	16530	1.12
4 ^a	MA	50/0.01	(Me) ₂ N/0.20	0.5	58	10004	13800	1.44
				1.5	83	14360	20000	1.25
5 ^a	MA	200/0.04	(Me) ₂ N/0.08	2.0	55	9470	13000	1.35
				5.0	78	13396	16950	1.28
6 ^a	MA	100/0.02	(Me) ₂ N/0.04	2.0	49	8402	12050	1.71
				6.0	77	13258	17750	1.46
7 ^b	MMA	100/0.02	dN/0.04	6.0	52	10676	12050	1.20
8 ^b	MMA	100/0.02	MeO/0.04	6.0	59	12097	13570	1.25
9 ^b	MMA	100/0.02	(Me) ₂ N/0.04	6.0	54	10976	13670	1.28
10 ^b	MMA	20/0.004	(Me) ₂ N/0.08	52	32	6522	8500	1.41

^a $[MA]/[EBiB]/[R-bpy]/[CuBr_2] = 200:1:X:Y$ with 5 cm copper wire in 50 (v/v) % DMSO at 25 °C. ^b $[MMA]/[EBPA]/[R-bpy]/[CuBr_2] = 200:1:X:Y$ with 1 cm copper wire in 50 (v/v) % 3:1 anisole/DMSO mixture at 60 °C.

polymerization via a linear increase in M_n with conversion, and M_w/M_n values <1.15 (Figure 1B). However, the most active (Me)₂N-bpy ligand resulted in low initiation efficiencies ($M_{n,GPC} \gg M_{n,theo}$) due to its high reactivity, producing large radical concentrations, and causing early termination events.

CV and normal ATRP experiments revealed that EDGs on bpy drastically influenced the polymerization behavior and confirmed an increase in the K_{ATRP} . Ligands with larger K_{ATRP} values should provide higher absolute $[Cu^{II}/L]$ in dilute conditions, permitting a CRP even in the presence of ppm catalyst concentrations. Typically when ppm catalyst concentrations are used, highly active Me₆TREN and TPMA ligands must be employed because complexes with low activity ligands (e.g., H-bpy) have been shown to be ineffective due to insufficient $[Cu^{II}/L]$.¹² Previous literature accounts have shown large M_w/M_n values result with bpy and other low activity ligands when polymerizing styrenes,¹² methacrylates,¹⁸ and acrylates.^{13,44} Therefore, our newly employed and highly active R-bpy ligands were investigated in their ability to maintain CRP behavior with ppm concentrations of catalyst.

Table 2 summarizes a variety of polymerizations using copper wire as a supplemental activator and a reducing agent with R-bpy ligands designed to study the influence of the R group, $[Cu^{II}]$, $[Cu^{II}/L_2]$, and monomer (i.e., MA and MMA).

Reaction conditions were utilized similar to previous literature reports.^{16,44–47} The first investigation was a comparison of dN, MeO, and (Me)₂N ligand substituents at 500 ppm of $[Cu^{II}]$. Similar to the observation with normal ATRP, ATRP conducted with 500 ppm of Cu^{II} showed that increasing EDG substituents resulted in higher rates of polymerizations (entries 1–3 at 2 h). Furthermore, polymers of similar M_n had lower M_w/M_n values when using more active catalysts (entries 1 (7 h), 2 (5 h), and 3 (2 h)). In particular, the medium activity dN-bpy provided a M_w/M_n value >1.7, whereas the newly employed (Me)₂N-bpy provided a M_w/M_n value of 1.12. Lower M_w/M_n values were obtained with larger K_{ATRP} ligand because they provide higher $[Cu^{II}/L]$, which increases the rate of deactivation resulting in fewer monomer additions in each activation–deactivation cycle.¹²

After establishing that the (Me)₂N-bpy was the most effective ATRP ligand under highly dilute conditions, the concentration limit was probed by varying the $[Cu^{II}]$ and $[Cu^{II}/L]$. Entries 3–4 represent identical polymerization conditions except with a 10-fold difference in the $[Cu^{II}]$. With only 50 ppm $[Cu^{II}]$, a rapid polymerization occurred, reaching >80% conversion in 1.5 h, while maintaining M_w/M_n values <1.3. It should be noted that between these two

experiments the concentration of ligand remained constant and only the concentration of Cu^{II} was decreased.

In a separate series of polymerizations, the concentration of Cu^{II} and ligand were systematically decreased, from 500 to 100 ppm of Cu^{II} (entries 3, 5, and 6). In this series, the concentration of ligand was always twice that of the copper (i.e., we use Cu/L rather than Cu/L₂ for nomenclature consistency). As the concentration of [Cu/L] was decreased, the polymerization rate also decreased. As evidenced in Table 2 (entries 3, 5, and 6 at 2 h), the conversion of monomer was 78, 55, and 48% for 500, 200, and 100 ppm of [Cu^{II}/L], respectively. Similar behavior was previously observed in literature when conducting ATRP in the presence of metallic copper with MMA and MA.^{18,44} In addition, larger concentrations of [Cu^{II}/L] yielded polymers with lower M_w/M_n values. From copper concentrations of 500 to 100 ppm (entries 3 (2 h) and 6 (6 h)), the M_w/M_n values changed from 1.12 to 1.46 at similar conversion values of 80%.

The last series of experiments carried out were intended to probe the ability of R-bpy ligands to catalyze the polymerization of MMA utilizing ppm catalyst concentrations. Different polymerization conditions were used for MMA, including a mixed solvent system, higher reaction temperatures, and a more active initiator (i.e., ethyl α -bromophenylacetate (EBPA)). Similar conditions were shown in literature^{18,48} to be effective (i.e., EBPA and anisole) for MMA. As shown in entries 7–9, three different ligands were employed using 100 ppm of copper catalyst. In each case similar conversion values, molecular weights, and M_w/M_n values were obtained. Each of the R-bpy ligands proved to be capable of catalyzing ATRP and provided polymers with low M_w/M_n values using only 100 ppm of Cu^{II}/L. Similar to other literature examples, very active catalyst system resulted in limited initiation efficiency in the polymerization of MMA.^{18,49} These experiments were then extended to a 20 ppm ATRP system employing the most active (Me)₂N-bpy ligand (Table 2, entry 10). This polymerization reached a lower catalyst limit resulting in a slow polymerization rate, reaching only 32% conversion in 52 h, and a larger M_w/M_n value of 1.41.

The rational design of ligands provides a powerful tool to manipulate and improve transition metal catalyzed ATRP. In this work, electron donating substituents on bpy-based ligands proved to greatly enhance catalytic activity in ATRP. CV experiments confirmed that increased strength of EDGs, as described by σ_p values, resulted in increased activity of ATRP complexes. This result was bolstered by increased polymerizations rates of MA with EDG substituents, while still producing polymers with narrow M_w/M_n values and predetermined molecular weights. At catalyst loadings of 500 ppm, (Me)₂N-bpy was found to be superior to other R-bpy ligands (i.e., improved rate and M_w/M_n), and with 50 ppm catalyst concentrations (Me)₂N-bpy was still capable of producing polymers with M_w/M_n values <1.3.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details, polymerization kinetics, and additional characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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