

Full Paper: Several copper complexes used successfully as the catalysts for atom transfer radical polymerization (ATRP) were studied by cyclic voltammetry in acetonitrile. These complexes include CuBr or CuCl complexed by 2,2'-bipyridine (bpy), 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy), 4,4'-di(*n*-nonyl)-2,2'-bipyridine (dnNbpy), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), *N,N*-bis(2-pyridylmethyl)octylamine (BPMOA), *N,N*-bis(2-pyridylmethyl)octadecylamine (BPMODA), tris[(2-pyridyl)methyl]amine (TPMA) and tris[2-(dimethylamino)ethyl]amine (Me₆TREN), respectively. It was found that the $E_{1/2}$ value for the redox couple Cu^I/Cu^{II} strongly

depends on the nature of the ligand and the halogen. As the number of coordination sites of the ligand increases, the reducing power of the corresponding Cu(I) complex also increases. With the same ligand, CuCl complexes usually have a lower redox potential than CuBr complexes. These general trends agree with the kinetic features of ATRP catalyzed by the corresponding complex, and a correlation between the redox potential and the apparent equilibrium constant of ATRP for methacrylate was observed. The possibility of using electrochemistry as a screening method for selecting ATRP catalysts is therefore further discussed.

Cyclic voltammetric studies of copper complexes catalyzing atom transfer radical polymerization

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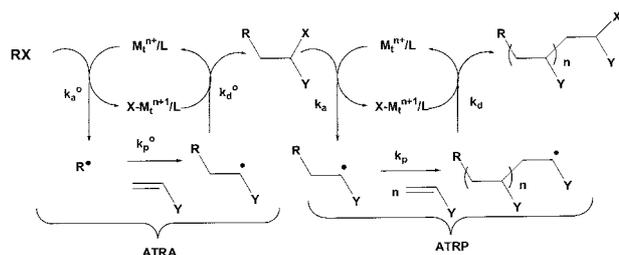
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Introduction

Atom Transfer Radical Addition (ATRA)^[1–4] and Atom Transfer Radical Polymerization (ATRP)^[5–8] are two powerful synthetic methods in organic chemistry and polymer chemistry, respectively. In ATRA, R-X (usually an organic halide) adds across the unsaturated carbon-carbon bond of an alkene, M, to form the monoadduct R-M-X in high yield, while ATRP achieves controlled/"living" radical polymerization of vinyl monomers by the repetitive ATRA process to form R-(M)_n-X, as shown in Scheme 1. Typically, the concentration of the radicals is much lower than the concentration of the metal complex deactivator due to the persistent radical effect,^[9] and therefore, the proportion of products formed by radical coupling and/or disproportionation can be neglected.

Transition metal complexes of Cu,^[10,11] Fe,^[12,13] Ru,^[14] Ni,^[15,16] etc. are usually applied to catalyze this process.

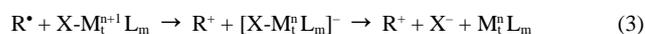


Scheme 1. Atom Transfer Radical Addition (ATRA) and Atom Transfer Radical Polymerization (ATRP).

The plausible mechanism for ATRA and ATRP involves a concerted inner-sphere electron transfer process (ISET, also called atom transfer) between the organic halide and the metal complex (Eq. 1). However, a two step process with an outer-sphere electron transfer (OSET) followed by halide migration is also possible (Eq. 2).



The mechanism can become more complex in some cases due to redox reactions induced by OSET and shown in Eq. 3–4.



Under such conditions, cationic or anionic intermediates may be generated, changing the radical nature of the process and consequently the products of the reaction. Therefore, choosing the appropriate catalytic system becomes extremely important to assure the control of the process.

The overall rate of ATRA and ATRP depends on the rate constant of addition of radical to monomer (propagation, k_p) but also on the equilibrium constant of the atom transfer process ($K_{eq} = k_a/k_d$, Eq. 5).

$$R_p = k_p [M][P^\bullet] = k_p [M][RX]_0 k_a [M_i^{n+1}] / (k_d [X-M_i^{n+1}]) \\ = k_p K_{eq} [M][RX]_0 [M_i^{n+1}] / [X-M_i^{n+1}] \quad (5)$$

Generally, equilibrium constants are larger for the more reducing complex, i.e. for systems that better stabilize the higher oxidation state of the metal species. Therefore, electrochemical measurements may be useful for the better understanding of ATRP processes and for the correlation of the catalyst structure with its reactivity and chemoselectivity. However, it has to be recognized that atom transfer process requires expansion of the coordination sphere of the metal complex, and the equilibrium is affected not only by the M_i^n/M_i^{n+1} electrochemical couple but also by the energetics of the $X-M_i^{n+1}$ bonding. Moreover, since organic radicals can be oxidized or reduced to cations and anions, the strongly reducing or oxidizing catalytic system may lead to the undesired side reactions. Additionally, the chemoselectivity of ATRA and the polydispersities of polymers prepared by ATRP may be affected by the dynamics of the electron transfer and atom transfer processes.

Previously, van Koten et al.^[17,18] studied the electrochemistry of arylnickel(II) complexes. They found that the redox potential of the complex was very sensitive to the para-substitution of the ligands and the counterion of the complex, which in turn strongly affected the catalytic behavior of the nickel complexes in ATRA reactions. We have also discussed the importance of OSET in ATRP and roughly correlated the activity of some catalysts with their electrochemistry based on the literature data.^[19] In this article, we report the electrochemical studies of several copper complexes used successfully as the catalysts for ATRP, in order to link their electrochemical properties with the kinetic feature of ATRP.

Experimental

Materials

CuCl (99.995+%, Aldrich) and CuBr (99.999%, Aldrich) were used as received. All ligands, except bpy (Aldrich), were synthesized according to the published procedure (structures are shown in Fig. 1).^[10,20,21] Acetonitrile was distilled over CaH_2 under argon. Supporting electrolyte, tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was synthesized by mixing aqueous solutions of NBu_4HSO_4 and NaBF_4 (Aldrich). The precipitate was extracted with dichloromethane and recrystallized from ethyl acetate/petroleum ether.

Cyclic voltammetric measurements

Cyclic voltammetry was performed at room temperature with a PGSTAT20 instrument, using GPES (General Purpose Electrochemical System) AutoLab software. Experiments were carried out in acetonitrile under argon, in a three-electrode cell connected to a Schlenk line. The counter electrode was a platinum wire of 1 cm^2 apparent surface area. The reference was a saturated calomel electrode (SCE) separated from the solution by a bridge (4 ml) filled with a 0.1 M

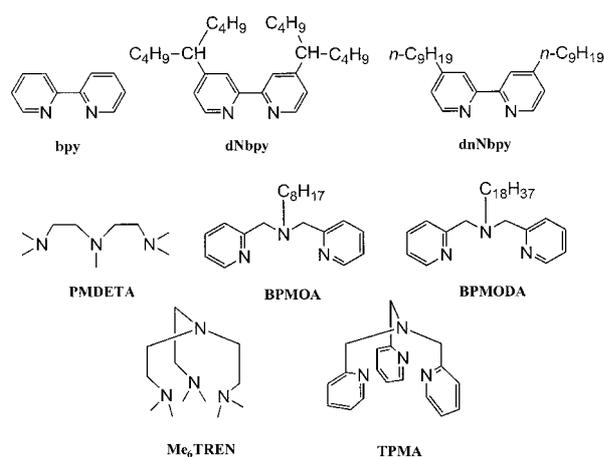


Fig. 1. Structures of the ligands of the copper complexes.

Bu_4NBF_4 solution in acetonitrile. A platinum electrode of 0.5 mm diameter was used as the working electrode. The scan rate ranged between 0.5 and $200\text{ V} \cdot \text{s}^{-1}$. The concentration of the copper complexes was kept at 0.01 M in all measurements.

Results and discussion

The objective of the electrochemical measurement has been to evaluate the effect of different ligands and halogen anions on the redox properties of copper complexes, and, potentially, to correlate their redox properties with their catalytic behavior in ATRP. For this reason, several commonly used ATRP catalysts were examined by cyclic voltammetry. The results are listed in Tab. 1.

General features

The voltammograms giving rise to the data reported in Tab. 1 correspond to one-electron chemically reversible couples, although their often large peak-to-peak separation indicates that the overall electrochemical processes behave as slow charge transfer. The only exception is the CuCl/TPMA complex where the peak-to-peak separation approaches the 60 mV canonical value for a Nernstian behavior. Such sluggish electron transfers (compare entries 3–6 in Tab. 1) point out to a profound reorganization of the coordination sphere of the copper center which is not surprising in view of the different preferred coordinations for each redox state (I or II) of the copper center. However, within the range of scan rates explored in this study, it was not possible to decide, if the reorganizations of the coordination environment are concerted with the electron transfer, or if they occur after the electron transfer step through a square scheme.^[22] Whatever is the exact situation, the half-sum of the oxidation and reduction potential peak afford an estimate of the $E_{1/2}$ characterizing the overall redox process (Tab. 1). Thus, although a quan-

Tab. 1. Redox potentials of several copper complexes measured by cyclic voltammetry in acetonitrile at room temperature.^{a)}

	Salt	Ligand	$E_{p,a}/V^{b)}$	$E_{p,c}/V^{b)}$	$E_{1/2}/V^{c)}$	$\Delta E_p/mV$	i_b/i_f^d	$E'_{p,c}/V^{e)}$
1	CuBr	bpy	0.145	-0.075	0.035	220	0.95	
2	CuCl	bpy	0.195	-0.135	0.030	330	0.78	
3	CuBr	dNbpy	0.295	-0.400	-0.050	695	0.57	-0.350
4	CuCl	dNbpy	0.320	-0.465	-0.070	785	0.49	-0.560
5	CuBr	dnNbpy	0.125	-0.250	-0.060	375	0.67	-0.215
6	CuCl	dnNbpy	0.185	-0.300	-0.055	485	0.69	-0.305
7	CuBr	BPMOA	0.070	-0.135	-0.035	205	0.73	
8	CuCl	BPMOA	-0.110	-0.250	-0.180	140	0.88	
9	CuCl	BPMODA	-0.060	-0.275	-0.170	215	0.67	-0.270
10	CuBr	PMDETA	-0.005	-0.140	-0.075	135	0.79	
11	CuCl	PMDETA	-0.105	-0.265	-0.185	160	0.78	
12	CuBr	TPMA	-0.200	-0.285	-0.245	85	0.73	
13	CuCl	TPMA	-0.290	-0.360	-0.325	70	0.76	
14	CuBr	Me ₆ TREN	-0.240	-0.355	-0.300	115	0.89	
15	CuCl	Me ₅ TREN	-0.350	-0.475	-0.413	125	0.72	

- ^{a)} Potentials referred to SCE electrode at a scan rate of 0.5 V s⁻¹. The ratio of salt/ligand is 1/2 for entries 1–6; 1/1 for entries 7–15.
^{b)} $E_{p,c}$ and $E_{p,a}$ are the peak potentials of the reduction and oxidation waves, respectively.
^{c)} $E_{1/2} = 1/2 (E_{p,c} + E_{p,a})$.
^{d)} i_b/i_f is the ratio of backward to forward peak current.
^{e)} Reduction potential of the Cu(II)L complexes obtained by mixing CuX₂ with the ligand L. Same conditions as for the voltammetric investigation of Cu(I) complexes.

titative analysis of the data could not be accomplished, a qualitative comparison may still meet the purpose of the current study.

Effect of ligand

The cyclic voltammograms of CuCl/L complexes are shown in Fig. 2 for L = bpy, PMDETA, TPMA and Me₆TREN. The redox potentials ($E_{1/2}$) of the copper complexes depend strongly on the structure of ligands. For example, by changing ligands from bpy to Me₆TREN, the redox potential of the corresponding complex decreased more than 300 mV (330 mV for the bromo derivative and 440 mV for the chloro one). This means that it is much easier to oxidize Cu(I)/Me₆TREN than Cu(I)/bpy. If the measured redox couple is associated with the atom transfer reaction, this big change in reducing properties may correspond to the ratios of the atom transfer equilibrium constant, K_{eq} , from 10⁴ to 10⁶ times, assuming identical structures of alkyl halide, RX and organic radical, R[•]:

$$\ln K_{eq} = nFE/RT, E = 0.06 \log K_{eq}$$

$$K_{eq} = k_a/k_d = ([R^{\bullet}]/[RX]) \times ([X-Cu(II)L]/[Cu(I)L]) \quad (6)$$

Starting from the ligand that forms the least powerful reducing agent, the general trend is: bpy < dNbpy or dnNbpy < BPMOA or BPMODA < PMDETA < TPMA < Me₆TREN. This trend is less clear for the bromo complexes than for chloro ones. For example, CuBr/BPMODA seems slightly less reducing than CuBr/dNbpy. This is perhaps due to the larger ΔE_p and then less precise $E_{1/2}$ values obtained for the two complexes.

The redox potential of the copper complex can be correlated with the structure of the ligand in several ways. For example, reducing power increases with the number of N-atoms: bidentate ligand < tridentate ligand < tripodal ligand. Also, the aliphatic amines which are more nucleophilic than aromatic amines better stabilize Cu(II) species: BPOMA < PMDETA; TPMA < Me₆TREN. It can be considered that Cu(II) is a stronger Lewis acid than Cu(I) and will complex better with stronger nucleophiles (trialkyl amines vs. pyridines).

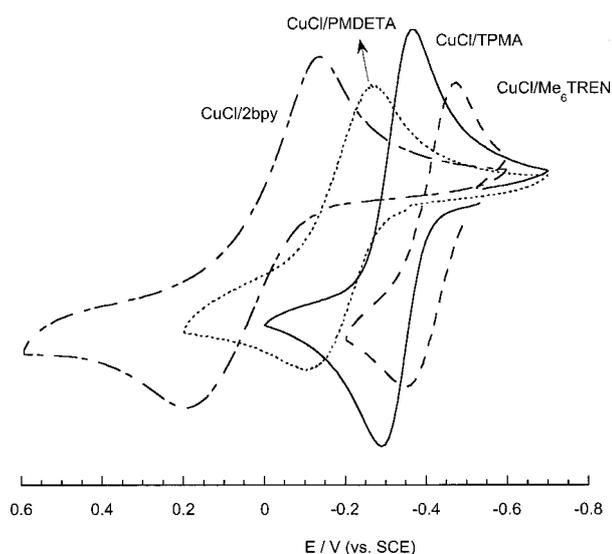


Fig. 2. Cyclic voltammograms of CuCl/2bpy, CuCl/PMDETA, CuCl/TPMA and CuCl/Me₆TREN in acetonitrile (0.1 M Bu₄NBF₄; scan rate: 0.5 V s⁻¹. [CuCl/L]₀: 0.01 M.

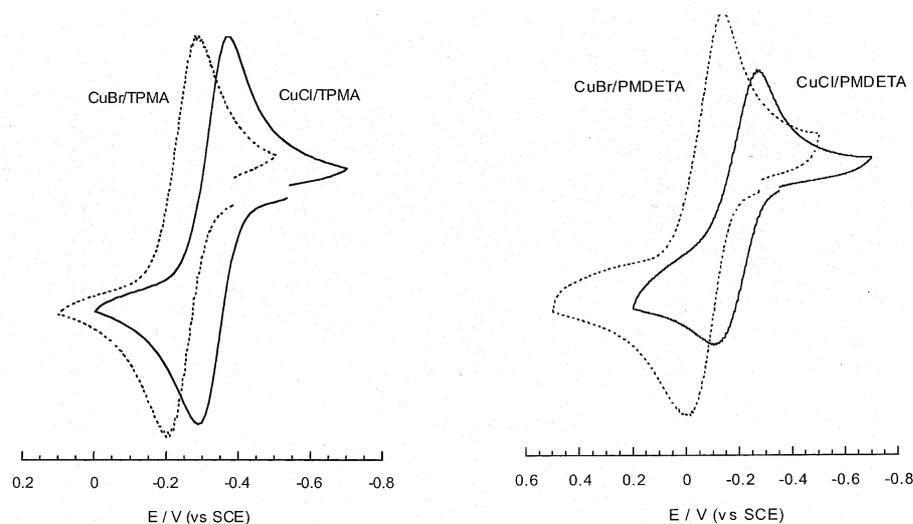


Fig. 3. Cyclic voltammograms of CuBr(Cl)/TPMA (left) and CuBr(Cl)/PMDETA (right) in acetonitrile (0.1 M Bu_4NBF_4 ; scan rate: 0.5 V s^{-1} . $[\text{CuCl/L}]_0$: 0.01 M.

Effect of the halogen

For a given ligand L, it was observed that the $E_{1/2}$ varied with the nature of the halide anion. CuCl complex usually displays a lower redox potential than CuBr complex, and the divergence is more pronounced with tridentate and tripodal ligands. In Fig. 3 two examples for the comparison between CuCl and CuBr with PMDETA or TPMA as the ligand are shown.

This variation of the redox potential with the nature of the halogen may indicate the involvement of the halide containing complex in the measured redox cycle, and hence reflect the difference in bonding energies of the halide ligand that coordinates to the copper center. The potential halide containing complexes can be X-Cu(I)L (for tridentate ligands only) or X-Cu(II)L^+ . If the latter species is involved, it is important to stress that it may not feature always the thermodynamically stable forms of the copper(II) species which are obtained by dissolution of the copper(II) salts with presence of the ligand. The voltammetric reduction peaks of authentic copper(II) solutions are generally observed at potentials which differ from the reduction peak associated to the oxidation of the Cu(I) species (Tab. 1). This is especially visible for the branched p-substituted bpy ligands (entries 3 & 4 in Tab. 1).

For relatively well defined redox cycles, the difference of $E_{1/2}$ between CuCl and CuBr complex is in the range of 100 mV. This may correspond to the 10–100 times higher equilibrium constant (K_{eq} , Eq. 6) of the CuCl complex to be oxidized. However, ATRP processes initiated by a RCl/CuCl/L system are generally slower than those initiated by RBr/CuBr/L . This discrepancy can be explained by the stronger C–Cl bonding compared to C–Br bonding, which overcompensates Cu–Br versus

Cu–Cl bonding. The different solubility of the copper complexes may also play a role.

Relationship with ATRP

As mentioned in the introduction, the most plausible mechanism of ATRP involves a series of inner sphere electron transfer processes. Hence, it is expected that the activity of the catalyst can be connected with its redox properties.

It has to be, however, recognized that kinetics of ATRP depends not only on the equilibrium and rate constants but also on the concentration of the activating cuprous species and deactivating cupric species (cf. Eq. 5). The cupric species, which could also be considered as persistent radicals,^[9] are formed spontaneously by the radical termination processes, meaning that, when the equilibrium constant is larger, more radicals are formed, they terminate more rapidly forming excess of Cu(II) and the reaction is slower than expected. In real polymerization systems the situation is more complex due to the effect of the chain length on termination rate coefficients,^[23] as well as limited solubility of some reagents. For example, although the polymerization of methyl methacrylate (MMA) with dNbpy as a ligand was much faster compared to styrene and methyl acrylate (MA),^[5] the opposite was found with PMDETA as a ligand, due to a much higher equilibrium constant, excessive termination and low solubility of the Cu(II)/PMDETA complex in the polymerization medium.^[24]

Nevertheless, in polymerization of acrylates in which equilibrium constants are relatively low and copper complexes dissolve quite well, a rough correlation between the composition of the catalysts and the overall rates can

Tab. 2. Bulk polymerization of methyl acrylate (MA) by ATRP. Catalyst: CuBr with different ligands.

Ligand	DNbpy	BPMOA	PMDETA	TPMA	Me ₆ TREN
Initiator	EBP	EBP	EBP	EBP	EBP
M/I	232	232	232	232	232
I/CuBr/L	1/1/2	1/1/1	1/0.2/0.2	1/0.2/0.2	1/0.1/0.1
Temp. (°C)	50	50	50	50	50
Time (h)	8	3.1	7.2	0.9	0.75
Conv. (%)	80	82	55	79	82
$\bar{M}_{n,th}$	15960	16320	10860	15800	16320
$\bar{M}_{n,sec}$	17470	14400	8170	15200	16920
\bar{M}_w/\bar{M}_n	1.27	1.12	1.21	1.05	1.07
$K_{eq}^{app} (M^{-1})^a$	8.9×10^{-7}	2.5×10^{-6}	2.6×10^{-6}	4.1×10^{-5}	1.0×10^{-4}
Ref.	[20]	[21]	This work	[21]	[20]
$E_{1/2}$ (V)	-0.052	-0.033	-0.072	-0.242	-0.298

a) K_{eq}^{app} is calculated as the slope of $-\ln(1 - \text{Conv}/100)$ vs. time plot divided by the propagation rate constant (k_p , assumed to be similar to that of butyl acrylate, which is $2.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 50°C),^[28,29] original concentrations of the initiator ($[I]_0$) and the catalyst ($[Cu^I]_0$), i.e.

$$K_{eq}^{app} = \frac{K_{eq}}{[Cu^{II}]} = \frac{d \ln([M]_0/[M])}{dt \cdot k_p \cdot [Cu^I]_0 \cdot [I]_0}$$

be proposed. Tab. 2 presents the kinetic data of bulk ATRP of methyl acrylate initiated by ethyl 2-bromopropionate (EBP) and catalyzed by various copper complexes.

Me₆TREN as a ligand gives the fastest polymerization among all the copper complexes tested, followed by TPMA, PMDETA, BPMOA and dNbpy. The polymerizations catalyzed by Cu(I)/Me₆TREN and Cu(I)/TPMA are so fast, that in order to achieve good control of the polymerization, the amount of the catalyst, as well as the reaction temperature (usually performed at room temperature) should be largely reduced.

Such ATRP kinetic behavior is in qualitative agreement with the redox potential values of the catalysts measured by cyclic voltammetric studies, as demonstrated in the plot of $\log(K_{eq}^{app})$ versus $E_{1/2}$ (Fig. 4). In Fig. 4, the *apparent* equilibrium constant ($K_{eq}^{app} = K_{eq}/[Cu^{II}]$, see the note for Tab. 2) was used instead of the equilibrium constant (K_{eq}) to evaluate the catalytic activity of each copper complex, since the equilibrium concentration of the Cu(II) complex which is necessary to calculate K_{eq} was only available for a few systems (dNbpy,^[25] PMDETA^[21] and BPMOA^[21]). The rough estimation of the apparent equilibrium constants were based on the assumption of an external first order with respect to both initiator and Cu(I) species.

The lower the redox potential, the larger the apparent equilibrium constant for the oxidation reaction of Cu(I) to Cu(II), and therefore the higher the activity in catalyzing the polymerization. The higher than expected $E_{1/2}$ and K_{eq}^{app} values for BPMOA, and the lower than expected values for dNbpy, respectively, may be ascribed to either low precision of $E_{1/2}$ or variable $[Cu^{II}]$ generated and dissolved in each catalytic system.

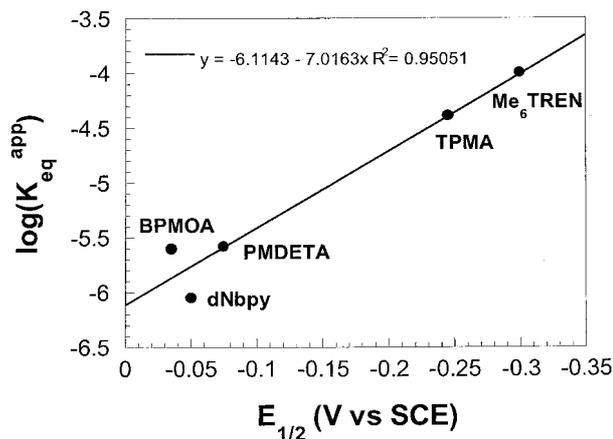


Fig. 4. Correlation between ATRP kinetics and the redox potentials of the CuBr complexes.

It may be interesting to compare the activity of copper complexes with other metal catalysts in ATRP based on their redox potentials. In Fig. 5 a redox potential chart of several metal complexes including Cu and Ni in various solvents is shown. The nickel complexes are successful ATRA catalysts, and some of them are also reported to catalyze ATRP, including Ni(NCN-H)Br shown in Fig. 5.^[16] The redox potential values are collected from literature data. Unfortunately, due to different solvents used for different complexes, it is not possible to make a quantitative comparison. Nevertheless, it appears that copper complexes generally have redox potential values comparable or lower than those of nickel complexes. This agrees with the reported ATRP kinetics. Copper-based complexes can be used for a variety of monomers, including methacrylates, styrenes and acrylates, and under mildest conditions (highest dilution, lowest temperature). Typically, Ni complexes can be applied only in ATRP of the most reactive monomers such as methacrylates. In addition, they require longer time to achieve high conversion,^[16] and sometimes they need an activator as well.^[15]

The observed parallel trend of ATRP kinetics and the redox potentials indicates that electrochemistry may indeed provide a screening window for ATRP catalysts. It seems that metal complexes with redox potentials in the range between -0.3 V and $+0.6 \text{ V}$ (versus NHE) may become useful ATRP catalysts in polymerisation of styrene and (meth)acrylates. When the redox potential is lower than -0.3 V , the catalytic reaction becomes too fast and may require special techniques for controlled polymerization, due to excessive radical termination. On the other hand, when the redox potential is higher than $+0.6 \text{ V}$, the polymerization rate is too slow to be practical. Furthermore, outer sphere electron transfer side reactions (Eq. 3 and Eq. 4) may readily occur and surpass the atom transfer reaction when the redox potential of the metal complex is too low or too high.

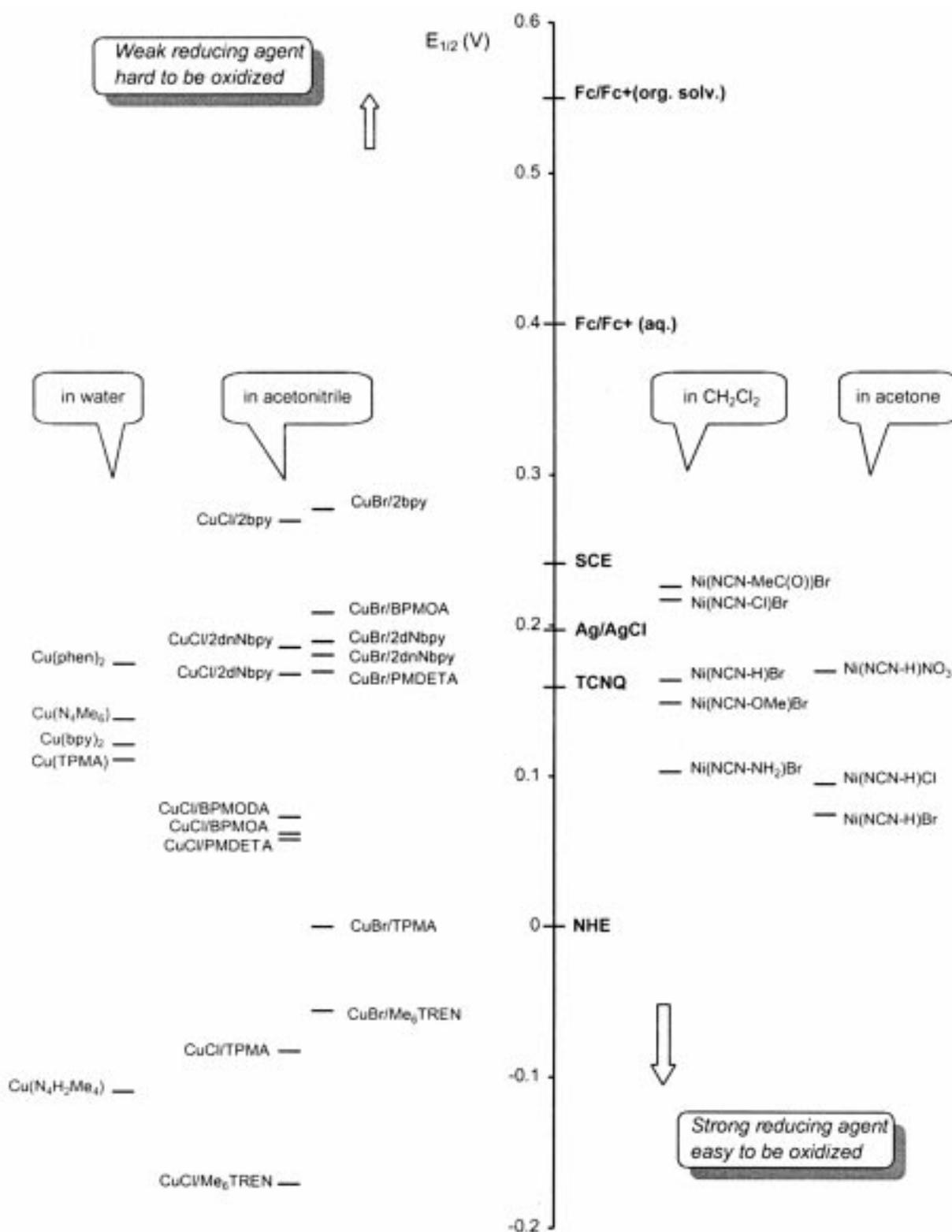


Fig. 5. Redox potentials of some metal complexes. Ref.: nickel complexes in acetone^[18] and CH₂Cl₂,^[17] copper complexes with linear tetramine ligands (Cu(N₄Me₆), Cu(N₄H₂Me₄))^[27] and other copper complexes in aqueous solution.^[26] The values of $E_{1/2}$ of the nickel complexes are calculated based on published data vs. Fc/Fc⁺ (0.55 V vs. NHE).

It should be emphasized that the cyclic voltammetric measurements in this study were carried out under conditions quite different from those of ATRP, especially in terms of the solvent and the temperature. Therefore, the measured redox potential can only be used as a reference in evaluating the activities of the metal complexes in ATRP. Moreover, redox potentials usually provide information on outer sphere electron transfer between the metal complex and the selected electrode. It may not be fully related to atom transfer reactions alone, which rather proceed through the inner-sphere electron transfer between the metal complex and an organic compound. How to correlate the two-electron transfer processes, both thermodynamically and kinetically more sufficiently, is a subject of a future investigation.

Conclusion

Several copper complexes that catalyze atom transfer radical polymerization successfully were studied by cyclic voltammetry. A general trend of the variation of redox potentials by changing the ligand and the anion was observed, and this trend is in agreement with the activities of the complexes in ATRP. This result indicates that an electrochemical approach can serve as a qualitative tool to select possible ATRP catalyst.

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