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Efficient Atom-Transfer Radical Polymerization of Methacrylates Catalyzed by Neutral Copper Complexes

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ABSTRACT: Copper homoscorpionate complexes Tp^{x}Cu(I)(NCMe) efficiently catalyze the Atom Transfer Radical Polymerization (ATRP) of methacrylate (MMA) and other methacrylates at 50 °C in the absence of any reducing agents. Plots of M_n vs monomer conversion are linear with low molecular weight distributions (M_w/M_n = 1.09) being obtained. The effects induced by the Tp^x ligand, the nature of the methacrylate substrate, the initiator and the temperature have been studied.

Introduction

The synthesis of polymeric materials by means of the atom transfer radical polymerization (ATRP) methodology has emerged in the last 15 years, mainly after the development of a series of very efficient catalysts by Matyjaszewski and co-workers in the mid 1990s.[1] It has been established[2] that the copper-catalyzed ATRP process initiates with an atom transfer radical addition (ATRA), a process that consists of the reaction of a metal complex with a halide compound (RX) to generate the radical $^{\bullet}$R and a metal halide complex ($k_{act,1}$, Scheme 1). The former radical reacts with the olefin to give a new radical, the abstraction of the halogen from the metal center taking place in the deactivation step ($k_{deact,1}$). As a result, the original metal specie is recovered and the desired addition product is formed. However, if the reaction conditions are modified, the ATRA reaction becomes the initiation step of ATRP. The use of organic halides as initiators allow the multiple olefin addition and the subsequent growth of a polymer chain. Thus, the homolytic cleavage of an alkyl halide bond by the metal complex generates alkyl radicals which can start the monomer polymerization (k_p), couple with another alkyl radical in a termination step (k_t) or be reversibly deactivated by the catalyst ($k_{deact,2}$). Generally, for ATRP, the structure of alkyl halide mimics the structure of monomer.

The undesired irreversible radical termination processes (k_t) are always present in ATRP reactions. For that reason, the equilibrium between the activation ($k_{act,2}$) and deactivation ($k_{deact,2}$) processes, $K_{ATRP} = k_{act,2}/k_{deact,2}$, must be shifted to the left ($k_{act,2} \ll k_{deact,2}$). Consequently, the intermediate radical concentration should be low (slow polymerization rate), the conversion should be limited, and the target molecular weight should be diminished. In addition, the irreversible radical−radical termination reactions resulted in the accumulation of the copper(II) complex or deactivator and because of it a high concentration of copper catalysts previously was required for ATRP and ATRA reactions. To surpass these drawbacks, different techniques had been developed in the past few years. One of them is the so-called ARGET[3] (activators regenerated by electron transfer), based in the addition of a reducing agent to regenerate the lower oxidation-state of the metal complex. In this sense, radical termination processes are usually minimized and ATRP reactions with lower catalyst concentrations can be carried out.

Efficiency of the catalyst in ATRP strongly depends on the nature of the metal as well as of the ligand. Although several metals have been described to catalyze ATRP reactions,[2,4] copper seems to be the metal of choice for these transformations,[5] due to the observation of high efficiencies with a broad range of monomers in diverse reaction media.[6] Most of the examples with this metal are based in cationic copper complexes, only a few catalytic[7,8] systems being based in the use of neutral Cu(I) complexes. This is in contrast with the need of soluble catalysts in the organic reaction media that could in principle be better achieved with a neutral Cu(I) complex.

With all these ideas in mind, we decided to investigate the potential of neutral copper(I) complexes containing the homoscorpionate ligands Tp^x (Table 1).[9] Previous work from our group has shown that some of these complexes efficiently catalyze ATRA[10] and ATRAC[11] (atom transfer radical addition and cyclization) reactions of halomethanes to several olefins. We are only aware of one previous example of the use of such complexes in ATRP processes, due to Matyjaszewski and coworkers.[8] The complex Tp*Cu (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) was employed as the catalyst precursor in a series of reactions using acrylates or styrene as the olefins. Although relevant results relative to mechanistic studies were obtained, polymerization with this complex was not well controlled, using both reverse and normal initiation.[12] Weight-average molecular weights (M_w) higher than predicted and broad molecular weight distributions (polydispersity index, PDI = M_w/M_n) were observed. Such poor control was attributed to a low deactivation rate constant.

The availability of different Tp^x ligands, in terms of electronic and steric properties, has allowed the tuning of the catalytic system based in Tp^{x}Cu(NCMe) complexes. In this contribution, we describe the use of Tp^{x}Cu(I)(NCMe) complexes as an efficient catalytic system for ATRP of various olefins, prefrerentially methacrylates (MMA, methyl methacrylate; EtMA, ethyl methacrylate; BuMA, *n*-butyl methacrylate; ^{t}BuMA, *tert*-butyl methacrylate), as well as acrylates (MA, methyl acrylate; BA, *n*-butyl acrylate) and styrene in the absence of any reducing agent.

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

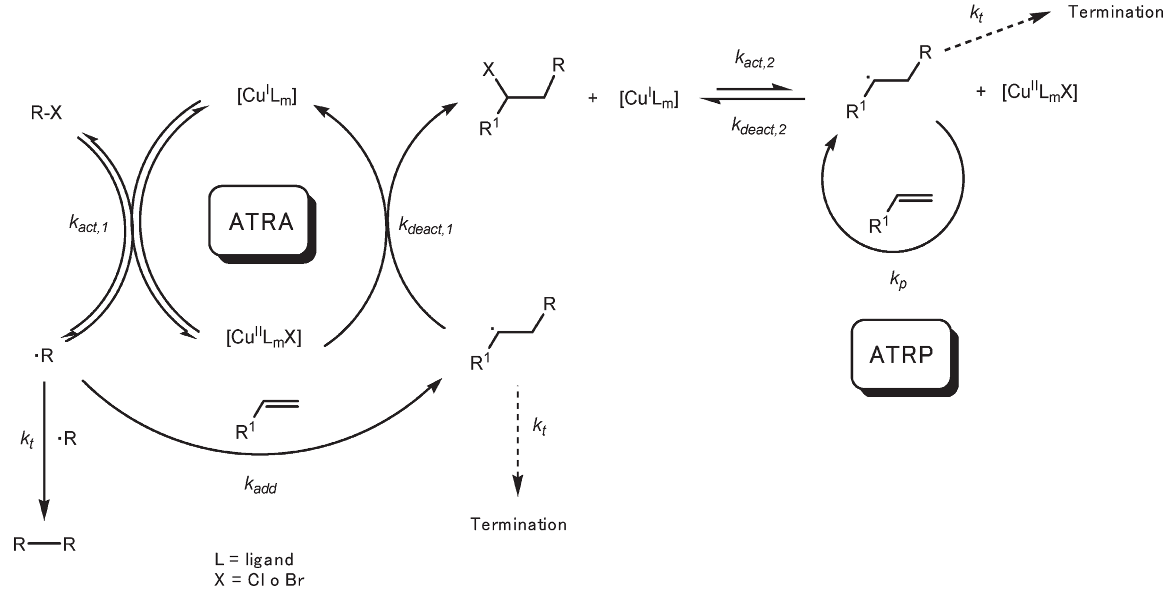
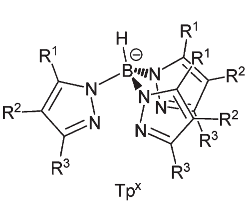


Table 1. Homoscorpionate Ligands Employed in this Work



$Tp^xCu(NCMe)$	R^1	R^2	R^3
$Tp^{Ph}Cu(NCMe)$ (**1**)	H	H	Ph
$Tp^{Cy,4Br}Cu(NCMe)$ (**2**)	H	Br	Cy
$Tp^{tBu,Me}$ Cu(NCMe) (**3**)	Me	H	^tBu
$Tp^{iPr_2}Cu(NCMe)$ (**4**)	^iPr	H	^iPr

Results and Discussion

$Tp^xCu(NCMe)$ Complexes as Catalysts for ATRP of Several Olefins. As a first set of experiments, we chose a series of representative $Tp^xCu(NCMe)$ complexes (Table 1) under two assumptions: (a) steric demand around the metal center is required to avoid catalyst decomposition and formation of $Tp^x{}_2Cu$ species and (b) high electron density at the metal center is also needed to reach the appropriate redox potential. The results obtained with complexes **1**−**4** as catalysts for polymerization of various monomers are shown in Table 2. Complexes **1** and **2** provided moderate to high conversions (64−98%) but with a low degree of control (PDI = 2.80−3.87). In all these cases, exothermicity was observed during the polymerization process, therefore the most likely reason for such poor control could be related to catalyst decomposition and subsequent free radical polymerization. To account for such decomposition, the lack of substitutents in R^1 could be invoked, since related decomposition pathways have been reported.[13]

After those results, we decided to use complex **3** as the catalyst precursor, containing the $Tp^{tBu,Me}$ ligand with the bulky ^tBu group as R^3 and a noticeable electron density at copper, as inferred from the ν(CO) value of 2059 cm^{-1} for the carbonyl adduct $Tp^{tBu,Me}Cu(CO)$). However, the results were not as good as expected (Table 2, entries 6−9). The polymerizations of acrylates (MA and BA) were not well controlled (entries 8−9) and the efficiency of the catalyst was low with monomer conversions of 41 and 30% for MA and BA, respectively. These results can be attributed to a large contribution of terminated chains, but also to an irregular growth of all the chains, which is accomplished with a slow reversible deactivation. On the contrary, complex **3** catalyzed the polymerization of MMA (entry 6) with an excellent control of the molecular weight distribution (PDI = 1.14). In this case, the reversible deactivation would be fast enough in comparison with the addition of the intermediate radicals to monomers, allowing a successful ATRP. However, a reaction time of 48 h in toluene at 50 °C was needed to reach 75% of monomer conversion. The origin of the slow polymerization rate could be based in steric factors: bulky substituents as R^3 might block the reversible activation. Accordingly, other authors have described similar results, reporting that exceeding the steric bulk at the metal center could make it less accessible for reaction with initiating and propagating centers, thus hindering halide abstraction.[14]

In order to slightly decrease the bulkiness of the group located at R^3 but maintaining the electronic density at the metal center we moved onto the Tp^{iPr2} ligand. Thus, when complex $Tp^{iPr2}Cu(NCMe)$ (**4**) was employed in the polymerization of MMA, 90% conversions where achieved at only 50 °C for 24 h (Table 2, entry 10), and with a remarkable control over the polydispersity (1.09). More interestingly, this transformation takes place in the absence of any reducing agent added. Under the same reaction conditions, methyl- and *n*-butyl acrylates were polymerized in moderate yields and with molecular weight distributions between 1.73 and 1.79 (entries 11−12). Finally, when styrene was used as monomer the conversion reached 55% at a reaction time of 48 h (entry 13). Although the temperature had to be increased up to 80 °C due to the low propagation rate constant of the intermediate radicals to styrene, a low molecular weight distribution (1.16) was obtained, indicating a controlled radical polymerization.

Effect of Monomer Structure. After establishing the excellent performance of the complex $Tp^{iPr2}Cu(NCMe)$ for the ATRP of MMA, a series of different methacrylates: methyl, ethyl, *n*-butyl, and *tert*-butyl methacrylate were screened as substrates leading to the results shown in Table 3.

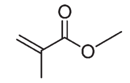
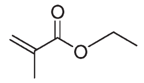
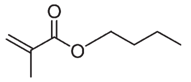
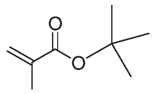
The degree of conversion strongly depends on the monomer structure and decreased in the order MMA > EtMA > BuMA > ^{t}BuMA, which in good accord with the steric effects of the Tp^{iPr2} ligands over the halide transfer during

Table 2. Atom Transfer Radical Polymerization (ATRP) of Different Monomers Using $Tp^xCu(NCMe)$ Complexes as Catalyst.[a]

entry	$Tp^xCu(NCMe)$	$[Tp^xCu]/[TsCl]/[M]^b$	monomer	t (°C)	time (h)	convn^c (%)	$M_{n,th}{}^d \times 10^{-4}$	$M_{n,GPC}{}^e \times 10^{-4}$	$M_w/M_n{}^f$
1	$Tp^{Ph}Cu(NCMe)$ (**1**)	1/2/300	BA	20	5	64	1.25	5.62	3.87
2		1/2/300	MA	20	5	84	1.10	7.40	3.77
3		1/2/300	MMA	20	48	70	1.07		ND
4	$Tp^{Cy,4Br}Cu(NCMe)$ (**2**)	1/2/1150	BA	20	2	90	6.65	5.89	2.80
5		1/2/1150	MMA	RT	12	98	5.66		ND
6	$Tp^{tBu,Me}Cu(NCMe)$ (**3**)	1/1/300	MMA	50	48	75	2.27	2.81	1.14
7		1/1/300	styrene	65	48	NR			
8		1/1/300	MA	50	48	41	1.08	13.86	1.90
9		1/1/300	BA	50	48	30	1.17	14.36	1.99
10	$Tp^{iPr2}Cu(NCMe)$ (**4**)	1/1/300	MMA	50	24	90	2.72	2.96	1.09
11		1/1/300	MA	50	30	60	1.57	22.29	1.79
12		1/1/300	BA	50	30	42	1.63	30.77	1.73
13		1/1/300	styrene	80	48	55	1.90	1.64	1.16

[a] Monomer/toluene = 1/1 (v/v). NR: no reaction. ND: not determined. [b] M: monomer. I: initiator (TsCl). [c] Conversion was determined by gravimetric analysis after desired times. [d] Number-average molecular weights: $M_{n,th}$ = ([monomer]$_0$/[TsCl]$_0$) × $M_{monomer}$ × convn (%) + M_{TsCl}; $M_{monomer}$ and M_{TsCl} are the molecular weights of the monomer and the initiator. [e] $M_{n,GPC}$ determined by gel permeation chromatography (GPC) using polystyrene standards. [f] M_w/M_n: molecular weight distributions or polydispersity index (PDI).

Table 3. Atom Transfer Radical Polymerization (ATRP) of Different Methacrylates Using $Tp^{iPr2}Cu(NCMe)$ Complexes as Catalyst.[a]

entry	monomer	conv (%)^b	$M_{n,th}{}^c \times 10^{-4}$	$M_{n,GPC}{}^d \cdot \times 10^{-4}$	$M_w/M_n{}^d$
1		90	2.72	2.96	1.09
2		87	3.00	2.73	1.09
3		81	3.47	3.26	1.09
4		57	2.45	2.77	1.08

[a] Temperature = 50 °C, initiator = TsCl, time = 24 h, monomer/toluene = 1/1 (v/v), and [$Tp^{iPr2}Cu(NCMe)$]/[TsCl]/[monomer] = 1/1/300. [b] The conversions were determined by gravimetric analysis. [c] $M_{n,th}$ = ([monomer]$_0$/[TsCl]$_0$) × $M_{monomer}$ × convn (%) + M_{TsCl}; $M_{monomer}$ and M_{TsCl} are the molecular weights of the monomer and the initiator. [d] M_w/M_n and $M_{n,GPC}$ determined by GPC using polystyrene standards.

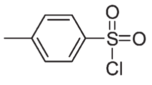
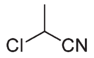
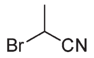
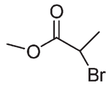
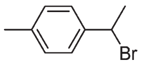
the activation and deactivation steps. The decrease observed in apparent polymerization rate depends on the equilibrium position of the atom transfer process. Shifting this equilibrium means affecting the activation and deactivation steps in a different manner. The molecular weight distributions obtained remain almost unchanged independently of the monomer used since these depend only on the ratio between propagation and deactivation rate constants.

Effect of Initiator. A well-known feature of these initiator-triggered transformations is that the control over the polymerization process can be improved by choosing the appropriate initiator.[15] A fast initiation step is required to ensure uniform polymer growth, although some considerations must be taken into account. For example, the R-X bond (X = Cl, Br) at the initiator has to be weak enough to promote a fast radical formation and also, the activation process at the initiation step must be as fast as the reactivation of the dormant chain to guarantee efficient generation of polymer chains. In addition, deactivation rate must be faster than activation and propagation rates to ensure a high concentration of the dormant species and therefore, minimizes the radical−radical termination process. The accomplishment of all these requirements usually provides well-defined polymers with low polydispersities.

The results obtained for the ATRP of MMA using complex **4** as catalyst at 40 °C for 24 h with five different initiators are shown in Table 4. *p*-Toluenesulfonyl chloride (TsCl), 2-chloropropionitrile (ClPN), 2-bromopropionitrile (BrPN), methyl 2-bromopropionate (MBrP) and 1-(1-bromoethyl)-4-methylbenzene (PEBr) were tested as initiators with variable success. Thus, when polymerization was carried out with bromide-containing initiators, broad molecular weigh distributions were obtained (1.21−1.48: entries 3−5) in comparison to those bearing chloride groups (1.09−1.10, entries 1−2). This behavior suggests that the deactivation of the intermediate radicals, by abstraction of the halogen atom from the copper(II) complex, is too slow in the case of bromide, giving rise to termination processes. In particular, when the reaction was performed under the same conditions and with the same initiator structure except the halide atom (entry 2 vs entry 3), the results showed a higher degree of conversion for BrPN as initiator, due to the weaker C−Br that provide fast initiation step. However, deactivation process during polymerization should be slower for the bromide case (due to the stronger Cu−Br affinity at Tp^xCuBr complex), inducing a higher concentration of intermediate radicals and subsequently leading to broad molecular weigh distributions caused by termination process.

The best conversion and molecular weigh distribution is obtained with TsCl as initiator (entry 1). Following that result, a study of the amount of the initiator was performed, using 1, 2, 4, and 10 equiv of TsCl with respect to the catalyst

Table 4. Atom Transfer Radical Polymerization (ATRP) of MMA Using Various Initiators Catalyzed by $Tp^{iPr2}Cu(NCMe)$ Complex.[a]

entry	initiator	conv (%)[b]	$M_{n,th}$[c] · 10^{-4}	$M_{n,GPC}$[d] · 10^{-4}	M_w/M_n[d]
1		80	2.40	2.26	1.07
2		81	2.45	1.81	1.10
3		89	2.69	2.45	1.21
4		98	2.96	3.55	1.48
5		99	2.97	2.97	1.34

[a] Temperature = 40 °C, time = 24 h, MMA/toluene = 1/1 (v/v), and $[Tp^{iPr2}Cu(NCMe)]/[initiator]/[MMA] = 1/1/300$. [b] The conversions were determined by gravimetric analysis. [c] $M_{n,th} = ([MMA]_0/[initiator]_0) \times M_{MMA} \times convn (\%) + M_{initiator}$; M_{MMA} and $M_{initiator}$ are the molecular weights of the monomer and the initiator. [d] M_w/M_n and $M_{n,GPC}$ determined by GPC using polystyrene standards.

Table 5. Atom Transfer Radical Polymerization (ATRP) of MMA Using Different Amounts of TsCl Catalyzed by $Tp^{iPr2}Cu(NCMe)$ Complex.[a]

entry	Tp^xCu:TsCl:MMA	convn (%)[b]	$M_{n,th}$[c] × 10^{-4}	$M_{n,GPC}$[d] × 10^{-4}	M_w/M_n[d]
1	1:1:300	90	2.72	2.96	1.09
2	1:2:300	74	1.13	1.66	1.34
3	1:4:300	68	0.53	0.79	1.40
4	1:10:300	57	0.19	1.37	1.82

[a] Temperature = 50 °C, initiator = TsCl, time = 24 h, and MMA/toluene = 1/1 (v/v). [b] Conversions were determined by gravimetric analysis. [c] $M_{n,th} = ([MMA]_0/[TsCl]_0) \times M_{MMA} \times convn (\%) + M_{TsCl}$; M_{MMA} and M_{TsCl} are the molecular weights of the monomer and the initiator. [d] M_w/M_n and $M_{n,GPC}$ determined by GPC using polystyrene standards.

(Table 5). The monomer conversion decreased and the molecular weigh distribution increased with the increase in the amount of TsCl. This suggests a low efficiency at initiation step presumably caused by the slow deactivation. An alternative explanation for these results could be that excess of RX shifts the ATRP equilibrium toward Cu(II) and radicals, also resulting in uncontrolled polymerization.

Kinetic Studies. We have monitored the conversions of the polymerization of MMA using complex **4** as the catalyst using two different initiators, with chloride (TsCl) and bromide (PEBr). Figure 1 shows the plots of $\ln[MMA]_0/[MMA]$ vs time as well as the dependence of M_n and polydispersity on the monomer conversion.

As shown in Figure 1a, first-order kinetics were observed from the plot of $\ln[MMA]_0/[MMA]$ vs time using TsCl as the initiator. Therefore, the catalyst exhibited high level of control over the polymerization process, as a consequence of the constant values of radical concentrations during the reaction. On the other hand, as depicted in Figure 1b, the experimental molecular weights of PMMA corresponded quite well with the theoretical values, indicating an efficient initiation step. In addition, the molecular weights distributions were relatively low ($M_w/M_n = 1.16$ to 1.07) throughout the reaction, showing the living nature of the polymerization reaction.

When the bromide-containing initiator was employed, again linear a correlation of $\ln([M]_0/[M])$ vs time was observed (Figure 1c). However, the polydispersities of the polymers obtained with TsCl were lower than those with PEBr. Therefore, the chloride-triggered polymerization exerts a better control of the molecular weight. It has been described in the case of cationic copper catalysts that halide exchange may occur between the initiator and the complex. Such exchange is not possible in the neutral complexes we are using herein, and consequently, the propagation step depends exclusively on the nature of halide from initiator R-X.

As shown in Figure 2, the MMA polymerization using complex **4** as the catalyst is faster with the bromide initiator ($k_{app} = 4.0 \times 10^{-5}$) compared to the chloride one ($k_{app} = 1.7 \times 10^{-5}$). This is in good agreement with a better initiation.[16] However, the polydispersity is better controlled by means of a facile deactivation step, that seems to be preferred for $Tp^{iPr2}Cu{-}Cl$. In case of $Tp^{iPr2}Cu{-}Br$, the deactivation rate is not fast enough to minimize the radical−radical termination process (Scheme 1).[17]

Effect of the Temperature on the ATRP of MMA. A series of experiments in which complex **4** was employed as the catalyst at four different temperatures (40, 50, 60, and 70 °C) was carried out to evaluate the effect of such variable. TsCl was chosen as the initiator, since it has been reported that less active initiators become more efficient at elevated temperatures.[18] As shown in Table 6 for conversion values, the catalytic activity of **4** increased with temperature. Thus, when the reaction was performed at 70 °C, 95% of monomer conversion was observed in 9 h with only a slight increase in the molecular weight distribution ($M_w/M_n = 1.14$). Actually, within the range of temperatures studied, low molecular distributions within the 1.07−1.14 interval were observed. As expected, the initial generation of radicals accelerates at higher temperatures and the stability of the catalyst (that does not decompose at those temperatures) allows a good control of the polymerization.

Effect of Solvent on ATRP of MMA. The selection of the appropriate solvent for ATRP processes can also be of importance, particularly with regards of the solubility of the catalyst precursor and the relative concentration of the Cu(I)/Cu(II) species.[19] However, coordinating polar

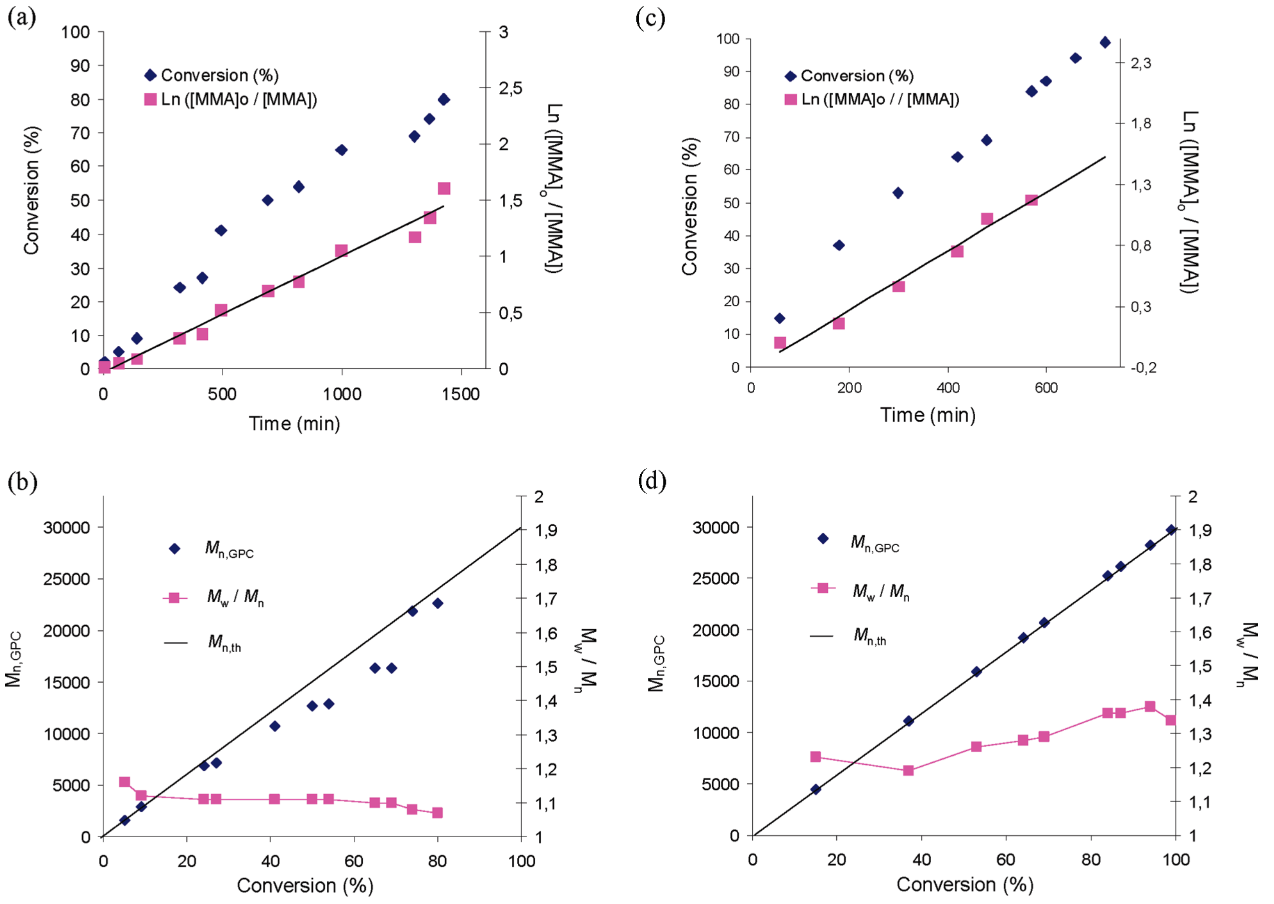


Figure 1. (a) Kinetics plots of ln[MMA]$_0$/[MMA] and MMA conversion versus reaction time using TsCl as initiator. (b) Dependence of molecular weights, M_n, and molecular weight distributions, M_w/M_n, on the monomer conversion for the atom transfer radical polymerization (ATRP) of MMA in toluene catalyzed by Tp^{iPr2}Cu(NCMe) complex at 40 °C, using TsCl as initiator. [MMA]$_0$ = 0.5 M; [Tp^{iPr2}Cu(NCMe)]$_0$/[TsCl]$_0$/[MMA]$_0$ = 1:1:300. (c) Kinetics plots of ln[MMA]$_0$/[MMA] and MMA conversion versus reaction time, using PEBr as initiator. (d) Dependence of molecular weights, M_n, and molecular weight distributions, M_w/M_n, on the monomer conversion for the ATRP of MMA in toluene catalyzed by Tp^{iPr2}Cu(NCMe) complex at 40 °C. [MMA]$_0$ = 0.5 M; [Tp^{iPr2}Cu(NCMe)]$_0$/[TsCl]$_0$/[MMA]$_0$ = 1:1:300, using PEBr as initiator.

Table 6. Atom Transfer Radical Polymerization (ATRP) of MMA at Different Temperatures Catalyzed by Tp^{iPr2}Cu(NCMe) Complex.[a]

entry	temperature (°C)	time (h)	convn (%)[b]	$M_{n,th}$[c] × 10^{-4}	$M_{n,GPC}$[d] × 10^{-4}	M_w/M_n[d]
1	40	24	80	2.40	2.26	1.07
2	50	24	90	2.72	2.96	1.09
3	60	15	94	2.84	2.69	1.16
4	70	9	95	2.87	2.71	1.14

[a] Initiator = TsCl, MMA/toluene = 1/1 (v/v), and [Tp^{iPr2}Cu(NCMe)]/[TsCl]/[MMA] = 1/1/300. [b] The conversions were determined by gravimetric analysis after desired times. [c] $M_{n,th}$ = ([MMA]$_0$/[TsCl]$_0$) × M_{MMA} × convn (%) + M_{TsCl}; M_{MMA} and M_{TsCl} are the molecular weights of the monomer and the initiator. [d] M_w/M_n and $M_{n,GPC}$ determined by GPC using polystyrene standards.

Table 7. Atom Transfer Radical Polymerization (ATRP) of MMA Using Different Amounts of Toluene Catalyzed by Tp^{iPr2}Cu(NCMe) Complex[a]

entry	MMA/toluene (v/v)	time (h)	convn (%)[b]	$M_{n,th}$[c] × 10^{-4}	$M_{n,GPC}$[d] × 10^{-4}	M_w/M_n[d]
1	1/0	5	74	2.24	1.86	1.12
2	1/1	24	90	2.72	2.96	1.09
3	1/2	24	67	2.03	1.91	1.09

[a] Temperature = 50 °C, and initiator = TsCl. [b] The conversions were determined by gravimetric analysis after desired times. [c] $M_{n,th}$ = ([MMA]$_0$/[TsCl]$_0$) × M_{MMA} × convn (%) + M_{TsCl}; M_{MMA} and M_{TsCl} are the molecular weights of the monomer and the initiator. [d] M_w/M_n and $M_{n,GPC}$ determined by GPC using polystyrene standards.

solvents such as DMF or acetone, among others, are of limited use in our Tp^{x}Cu due to their coordination to the metal center, as previously described for the related catalytic ATRA system.[10] Nevertheless, due to the excellent solubility of complex **4** in toluene or even in pure monomer, the influence of the polarity of the media in the ATRP of MMA has been investigated varying the ratio toluene/monomer. As shown in Table 7 (entry 1) when reaction was carried out in pure monomer, a 74% consumption of the monomer was observed in only 5 h. The rate decrease observed when more toluene is used maybe due to the decrease in polarity and/or of monomer concentration. On the other hand, it seems that the variation of the polarity of the reaction medium does not play a perceptible effect in the control of the molecular weigh distributions in the ATRP reactions catalyzed by **4**. The absence of influence of the

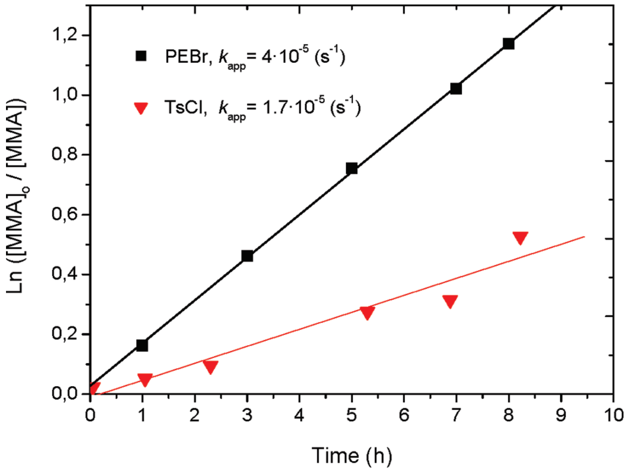


Figure 2. Kinetics plots for the polymerization of MMA at 40 °C catalyzed by complex **4** using TsCl or PEBr as initiators.

solvent polarity is in good agreement with an inner-sphere electron transfer for both activation and deactivation redox steps.[20]

Conclusion

The studies carried out have shown that subtle structural changes in the Tp^x ligand induce large differences in the catalyst activity of the Tp^{x}Cu complexes toward ATRP reactions. Successful results have been obtained when Tp^x ligand meets the following requirements: (i) bulkiness, in the R^3 group, therefore the formation of Tp$^x{}_2$Cu(II) complexes is avoided; (ii) substituents in R^1 position also prevents ligand decomposition, even at high temperature; (iii) alkyl groups as substituents favor the oxidation process in the activation step. These issues have made the ligand Tp^{iPr2} as the most convenient, and subsequently the complex Tp^{iPr2}Cu(NCMe) (**4**) has been found to catalyze the ATRP of methacrylates with good to high degrees of conversion as well as with low PDI values. More importantly, this system operates in the absence of any added reducing agent.

Experimental Section

General Information. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. Number- and weight-average molecular weights (M_n and M_w) and molecular weight distributions (polydispersity index, PDI = M_w/M_n) of each polymer were obtained by gel permeation chromatography (GPC) on a Waters GPC system, equipped with a Waters 515 HPLC pump, a Waters 2414 refractive index detector, and Styragel HR 5E 7.8 × 300 mm column (effective molecular weight range 10^3-10^7, pore size 5 μm). HPLC grade THF was used as the eluent at 40 °C, delivered at a flow rate of 1.0 mL·min^{-1}. Polystyrene standards obtained from Waters Co. were used to generate the calibration curve.

Materials. Olefins were purchased from Aldrich, distilled under reduced pressure, stored in a freezer under nitrogen, and filtered on neutral alumina columns prior to use: styrene (99%), methyl acrylate (MA, 99%), *n*-butyl acrylate (BA, 99%), methyl methacrylate (MMA, 99%), ethyl methacrylate (EtMA, 99%), *n*-butyl methacrylate (BuMA, 99%), *tert*-butyl methacrylate (^{t}BuMA, 99%). Toluene (99.8%) was dried over molecular sieves, degassed and stored under nitrogen. The homoscorpionate ligands were prepared according to literature methods[10] as well as the complexes Tp^{x}Cu.[15−18] Initiators were used as received: *p*-toluenesulfonyl chloride (TsCl, 98%), 2-bromopropionitrile (BrPN, 98%), ethyl 2-bromoisobutyrate (EtBriB, 99%), methyl 2-bromopropionate (MBrP, 98%), 2-chloropropionitrile (ClPN, 95%), 1-(1-bromoethyl)-4-methylbenzene (PEBr, 97%), ethyl bromo(phenyl)acetate (EBPA, 97%).

General Procedures for Polymerization. The following general procedure for polymerization reactions was employed in all cases. A solution of the olefin (9.35 mmol) and the corresponding Tp^{x}Cu complex (0.031 mmol from a toluene stock solution) were dissolved in the required amount of toluene to a total volume of 2 mL. The solution was transferred into a Schlenk flask and sealed with a rubber septum. The Schlenk flask was removed from the glovebox and placed in an oil bath at 50 °C. The solution was stirred for 10 min, the desired amount of the initiator (0.031 mmol) from a toluene solution was added via syringe and the flask was sealed with a glass cap. After 24 h of stirring at the desired temperature, all volatiles were removed under vacuo and polymer was dried for 24 h. Conversion was determined by gravimetric analysis previously to the GPC molecular weight analysis.

Synthesis of Poly(methyl methacrylate) by ATRP. In a typical procedure to synthesize PMMA, a Schlenk flask (15 mL) with a magnetic stir bar was charged with complex **4** (0.031 mmol, 100 μL from a toluene stock solution), methyl methacrylate (1.00 mL, 9.35 mmol) and toluene (0.80 mL) as the solvent. The Schlenk flask was removed from the glovebox and placed in an oil bath at 50 °C. The solution was stirred for 10 min, the desired amount of TsCl (0.031 mmol, 100 μL from a toluene stock solution) was added via syringe and the flask was sealed with a glass cap. After 24 h of stirring at 50 °C, all volatiles were removed under vacuo and resulting polymer was dried for 24 h. Conversion was determined by gravimetric analysis. Yield: 90%. A sample of the product was analyzed by GPC: $M_{n,GPC}$ = 2.96 × 10^4, $M_{w,GPC}$ = 3.23 × 10^4, M_w/M_n = 1.09. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 3.50−3.25 (3H, $-$OCH_3), 1.90−1.40 (2H, $-$CH_2C$-$), 1.25−0.50 (3H, $-$CCH_3). ^{13}C{^{1}H} NMR (400 MHz, CDCl$_3$, ppm): δ 178.1−175.8 ($-$*C*OOCH$_3$), 54.8−52.0 ($-$*C*H$_2$C$-$), 51.5 ($-$O*C*H$_3$), 45.4−43.8 ($-$*C*CH$_3$), 19.0−15.6 ($-$C*C*H$_3$).

General Procedure for Polymerization Kinetics. Polymerizations kinetics were conducted in an analogous manner to that described above, with a 10-fold scale-up. At the desired times, 0.5 mL aliquots were collected and transferred to Schlenk flasks. Workup of each sample was done as above. The conversion was determined by ^{1}H NMR spectroscopy before GPC analyses were carried out.

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Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra of polymer samples as well as GPC chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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