Tuning of ruthenium *N*-heterocyclic carbene catalysts for ATRP†

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Depending on the substituents, R^1 and R^2, ruthenium(II)–*p*-cymene complexes bearing *N*-heterocyclic carbene ligands are either efficient catalysts for the well-controlled atom transfer radical polymerisation of methyl methacrylate and styrene, or promote a redox-initiated free-radical process.

One of the most significant advances in controlled polymerisation over the past few years has been the development of transition-metal based catalysts for atom transfer radical polymerisation (ATRP). Following the seminal observations by Sawamoto[1] and Matyjaszewski[2] that ruthenium(II) and copper(I) complexes afforded highly efficient ATRP catalysts, a number of different metal ligand combinations were investigated.[3]

We have studied the utilisation of $RuCl_2$(*p*-cymene)(PCy_3) and of the Grubbs' ruthenium–benzylidene complex, $RuCl_2$(=CHPh)(PCy_3)$_2$, for ATRP of vinyl monomers.[4] We then became interested in related Herrmann–Grubbs complexes, $RuCl_2$(=CHPh)(L)(L′), bearing one or two *N*-heterocyclic carbene ligands (NHCs), L and L′, instead of tricyclohexylphosphine.[5] Nowadays, NHCs constitute a promising new class of ligands available for catalyst engineering and fine tuning, since their electronic and steric properties are liable to ample modification simply by varying the substituents on the nitrogen ring. Hence, we have launched a detailed investigation on the role of the NHC ligand in ruthenium–*p*-cymene catalyst precursors for the ring-opening metathesis polymerisation (ROMP) of cyclic olefins.[6] We now report on the use of new ruthenium catalysts bearing various NHC ligands for ATRP of vinyl monomers. We show that either well-controlled polymerisations of methyl methacrylate and styrene or competitive redox-initiated free-radical processes are promoted, depending on the substituents, R^1 and R^2, of the carbene ligand.

In a first set of experiments, the homogeneous ATRP of methyl methacrylate (MMA) initiated by ethyl 2-bromo-2-methylpropionate and ruthenium-NHC complexes was inves-

	R^1	R^2
1	Mes	Me
2	Mes	H
3	Mes	Cl
4	Cy	Me
5	Cy	H
6	Cy	Cl
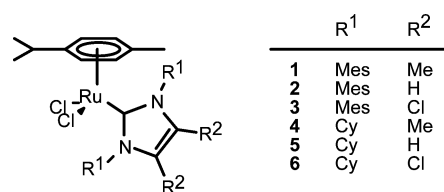
Cy = cyclohexyl; Mes = 2,4,6-trimethylphenyl

tigated at 85 °C under an inert atmosphere (Table 1). Complexes **2** and **3** with R^1 = mesityl and R^2 = H (**2**) or Cl (**3**) were more efficient than those having different R^1,R^2 combinations. The semilogarithmic plot of $\ln([M]_0/[M])$ *vs.* time† was linear in both cases with a pseudo-first order rate constant (k_{app}) of 10.6 $\times 10^{-6}$ s^{-1} for **2** and 3.85×10^{-6} s^{-1} for **3**, indicating that the radical concentration remained constant throughout the polymerisation run. With both complexes **2** and **3**, the molecular weights increased linearly with conversion, thus demonstrating good control over M_n. Polydispersities (M_w/M_n) were quite low (typically *ca.* 1.3) and decreased with monomer conversion (Fig. 1). By contrast, complex **1** displayed an induction period† after which the semilogarithmic plot was almost linear ($k_{app} = 16.4 \times 10^{-6}$ s^{-1}). Furthermore, M_n did not increase linearly with conversion and did not agree with theoretical values.

With styrene, complex **5** was the most efficient catalyst among those investigated. The polymerisation was well controlled as indicated by the linearity of the plots of $\ln([M]_0/[M])$ *vs.* time and of M_n *vs.* conversion.† Again, other R^1,R^2 combinations resulted in poorly or uncontrolled polymerisations. Indeed, replacement of hydrogens by methyl groups on both olefinic carbons of the NHC ligand in **5** dramatically changed the mechanism. With complex **4**, the semilogarithmic plot of $\ln([M]_0/[M])$ *vs.* time was no longer linear, and M_n as well as M_w/M_n remained constant (≈ 55000 and 1.9, respectively) throughout the run. A similar trend was observed for the polymerisation of MMA using **5** ($M_n \approx 35000$ and $M_w/M_n \approx 1.75$), indicating that both reactions were most probably taking place through a redox-initiated free-radical process.

Noteworthily, the switch from cyclohexyl to mesityl groups on both nitrogens of the carbene ligand (complexes **1–3**) caused

Table 1 Experimental data for the polymerisation of methyl methacrylate and styrene catalysed by ruthenium complexes **1–5**

Complex	$T_D{}^c$/°C	$E_{ox}^o{}^d$/mV	$\Delta E_p{}^e$/mV	PMMA^a				PS^b			
				Yield (%)	$M_n{}^f$	$M_w/M_n{}^f$	f^g	Yield (%)	$M_n{}^f$	$M_w/M_n{}^f$	f^g
1	210	370	90	28	52000	1.6	0.2	66	53000	1.75	0.5
2	—^{h}	450	—^{i}	49	28000	1.35	0.7	51	28000	1.8	0.7
3	162	610	110	24	12900	1.33	0.75	10	10200	1.9	0.35
4	170	470	—^{i}	94	160000	2.45	0.25	77	53000	1.9	0.55
5	190	630	80	51^j	36000	1.75	0.55	86	47000	1.25	0.7

^{a} Reaction conditions: $[MMA]_0 : [\text{initiator}]_0 : [Ru]_0 = 800 : 2 : 1$ (initiator, ethyl 2-bromo-2-methylpropionate; temperature, 85 °C; reaction time, 16 h); ^{b} Reaction conditions: $[\text{styrene}]_0 : [\text{initiator}]_0 : [Ru]_0 = 750 : 2 : 1$ (initiator, (1-bromoethyl)benzene; temperature, 110 °C; reaction time, 16 h); ^{c} Temperature at which the *p*-cymene ligand was released from the ruthenium complex as determined by TGA; ^{d} Oxidation potential; ^{e} Peak separation; ^{f} Determined by size-exclusion chromatography (SEC) with PMMA and PS calibration, respectively; ^{g} Initiation efficiency $f = M_{n,\text{theor.}}/M_{n,\text{exp.}}$ with $M_{n,\text{theor.}} = [\text{monomer}]_0/[\text{initiator}]_0) \times M_w(\text{monomer}) \times \text{conversion}$; ^{h} Broad thermogram ranging from 140 to 200 °C, and culminating between 165 and 185 °C; ^{i} Irreversible redox couple; ^{j} Ref. 8.
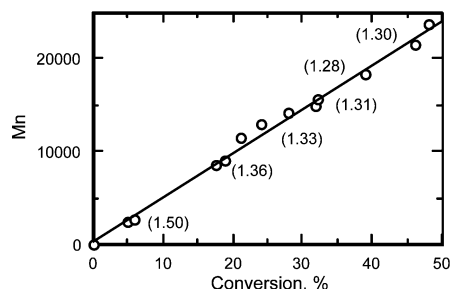
Fig. 1 Evolution of PMMA molecular weight, M_n, and polydispersity, M_w/M_n, with monomer conversion (complex **3**, $y = 292.96 + 479.13x$; $r^2 = 0.993$. See Table 1 for reaction conditions).

styrene metathesis to occur competitively with polymerisation. *Cis*- and *trans*-stilbene (the latter isomer being largely predominant) were formed in varying quantities according to the R^2 substituents. With complex **3** ($R^2 = Cl$) olefin metathesis was favoured (70% yield based on styrene), whereas with **1** ($R^2 = Me$) and **2** ($R^2 = H$) stilbene formation accounted for 25 and 5% of the monomer conversion, respectively. Interestingly, complexes **4** and **5** bearing *N*-cyclohexyl-substituted NHC ligands were devoid of any significant activity for the metathesis of styrene. Thus, with both MMA and styrene, subtle modifications of the R^2 substituents led to dramatic changes in the ability of the resulting ruthenium complex to control ATRP. For the polymerisation of methyl methacrylate, chlorine- and hydrogen-substituted NHCs led to equipotent catalytic systems, which were much more efficient than their methyl-substituted analogue. Spurred by this observation, we aimed at preparing complex **6** with R^2 chloro substituents for testing it in the ATRP of styrene. However, our attempts to synthesise the required free carbene ligand ($R^1 = Cy$, $R^2 = Cl$) using the same experimental procedure[7] that afforded the NHC with $R^1 = Mes$ and $R^2 = Cl$ failed.‡

In order to gain further insight into the catalytic process, the redox potentials and reversibilities of the various ruthenium complexes were determined by cyclic voltammetry (Table 1).§ Complexes **1**, **3**, and **5** gave rise to accessible and reversible one-electron redox couples [peak separation, ΔE_p(complex) 90, 110, and 80 mV, respectively] which compare with a value of 80 mV for ferrocene. Complexes **2** and **4**, on the other hand, displayed irreversible redox couples, in apparent contradiction with the polymerisation results. Indeed, complex **2** catalysed a well-controlled ATRP of MMA, whereas **4** and **5** promoted the redox-initiated free-radical polymerisation of styrene and MMA. Comparison of the oxidation potentials, E_{ox}^o, of complexes **3** and **5** posed an additional problem. Although their E_{ox}^o (610 and 630 mV, respectively) and $E_{\frac{1}{2}}$ (665 and 670 mV, respectively) were quite similar, complexes **3** and **5** displayed different abilities to control ATRP, suggesting that $E_{\frac{1}{2}}$ is not necessarily predictive of the catalyst's efficiency for ATRP with this particular series of complexes.[9] Steric and/or conformational constraints around the ruthenium atom may explain this discrepancy. A more likely explanation, however, is that cyclic voltammetry experiments were performed on well-defined ruthenium complexes and not on the actual catalytic active species which are devoid of the *p*-cymene ligand.

Ruthenium–*p*-cymene complexes (**1–5**) are 18-electron species, and it was demonstrated in different instances[10,11] that disengagement of the arene ligand is a prerequisite for their catalytic activity. Thermogravimetric measurements (Table 1) revealed that the temperature at which the *p*-cymene ligand was liberated also markedly depended on the substituents R^1,R^2: the lowest value (162 °C) was recorded with complex **3**, while the highest one (210 °C) was measured for complex **1**. *p*-Cymene

release was also evidenced by ^{1}H-NMR spectroscopy at 85 °C. The stability order of complexes **1–5** established in toluene-d_8 corroborated the one determined by TGA. With this in mind, the occurrence of an induction period in the polymerisation of MMA by complex **1**† can be attributed to a slow generation of the catalytically active species in the reaction mixture. So far, the precise nature of the catalytic species involved in these processes is unknown.

In conclusion, the complexes described here are fine examples of readily accessible ruthenium *N*-heterocyclic carbene catalysts, which are much more versatile in ATRP than $RuCl_2$(arene)(PR_3)[4] and $RuCl_2$(=CHPh)(PR_3)$_2$[5] derivatives. Fine tuning of their steric, electronic, and solubility parameters, as well as judicious choice of a compatible radical initiator are expected to yield even more active and well-controlled polymerisation systems. Further work is in progress to examine these features and their effect on the polymerisation of methyl methacrylate, styrene, and other monomers.

Notes and references

‡ Preliminary investigations showed that the reaction of 1,3-dicyclohexylimidazol-2-ylidene with 2 equiv. of CCl_4 in THF afforded a mixture of 1,3-dicyclohexyl-2-chloroimidazolium chloride and another, as yet unidentified, product instead of the expected 4,5-dichloro-1,3-dicyclohexylimidazol-2-ylidene.

§ Cyclic voltammetry analyses were performed in CH_2Cl_2, under nitrogen, using a Pt counter and working electrode, and an Ag/AgCl reference electrode with [${}^nBu_4N$][PF_6] as an electrolyte. The $E_{\frac{1}{2}}$ values for the ruthenium complexes were calculated *vs.* Fc/Fc$^+$ (0.55 V *vs.* Ag/AgCl) with $\Delta E_p = 80$ mV.

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