Ruthenium Alkylidenes: Modulation of a New Class of Catalysts for Controlled Radical Polymerization of Vinyl Monomers

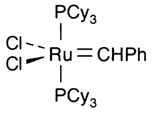
François Simal,[a] Sébastien Delfosse,[a] Albert Demonceau,*[a] Alfred F. Noels,[a] Karin Denk,[b] Florian J. Kohl,[b] Thomas Weskamp,[b] and Wolfgang A. Herrmann[b]

Abstract: Air-stable and readily available ruthenium benzylidene complexes of the general type [$RuCl_2$(=CHPh)(L)(L′)] (L, L′ = PCy_3 and/or *N*-heterocyclic carbene) constitute a new class of catalyst precursors for atom-transfer radical polymerization (ATRP) of methyl methacrylate and styrene, and provide an unprecedented example for the involvement of ruthenium alkylidenes in radical reactions. They promote the polymerization of various monomers with good to excellent yields, and in a controlled way with methyl methacrylate and styrene. Variations of their basic structural motif provide insights into the essential parameters responsible for catalytic activity. The ligands L (PCy_3 and/or *N*-heterocyclic carbene) turned out to play a particularly important role in determining the rate of the polymerizations. A similarly pronounced influence is exerted by the substituents on the *N*-heterocyclic carbene. Our results indicate that the catalysts decompose quickly under ATRP conditions, and polymerizations are mediated by both [$RuCl_2$(=CHPh)(L)(L′)] complexes and ruthenium species bereft of the benzylidene moiety, through a pathway in which both tricyclohexylphosphane and/or *N*-heterocyclic carbene ligands remain bound to the metal center. Polymerization of *n*-butyl acrylate and vinyl acetate is not controlled and most probably takes place through a redox-initiated free-radical process.

Keywords: carbenes · homogeneous catalysis · polymerizations · radical reactions · ruthenium

Introduction

With the isolation of the first stable carbene in 1988,[1] the chemistry of nucleophilic carbenes has experienced an incredible renaissance, which rapidly opened up new vistas in coordination chemistry and in homogeneous catalysis with organometallic compounds.[2] *N*-heterocyclic carbenes (NHC) of the imidazole and triazole type act as controlling ligands in catalysis, and their key advantages appear to be their easy synthesis and their increased Lewis basicity compared to phosphanes. Furthermore, *N*-heterocyclic carbenes may allow a fine tuning of the reactivity pattern of the catalytic species by systematic variations of their substituents. These concepts have been nicely illustrated, inter alia, in olefin metathesis catalyzed by ruthenium alkylidene complexes **1**–**3**.[3]



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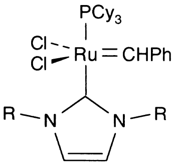
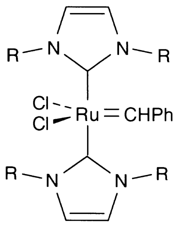
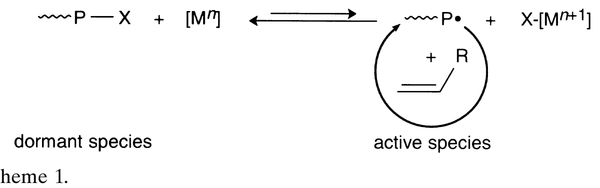


2a (R = Cy)
2b (R = (*S*)-CH(CH_3)Ph)



3a (R = Cy)
3b (R = *i*Pr)

Atom-transfer radical polymerization (ATRP) is so far one of the most successful approaches for controlling radical polymerization.[4] ATRP is based on a dynamic equilibration between the propagating radicals and the dormant species; this is established through the reversible transition metal-catalyzed cleavage of the covalent carbon–halogen bond in the dormant species (Scheme 1). Polymerization systems



Scheme 1.

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[a] Prof. Dr. A. Demonceau, Dr. F. Simal, S. Delfosse, Prof. Dr. A. F. Noels
Laboratory of Macromolecular Chemistry and Organic Catalysis
University of Liège, Sart-Tilman (B.6a), 4000 Liège (Belgium)
Fax: (+32) 4-366-3497
E-mail: a.demonceau@ulg.ac.be

[b] K. Denk, Dr. F. J. Kohl, Dr. T. Weskamp, Prof. Dr. W. A. Herrmann
Anorganisch-Chemisches Institut
Technischen Universität München
Lichtenbergstrasse 4, 85747 Garching bei München (Germany)
Fax: (+49) 89-289-13473
E-mail: lit@arthur.anorg.chemie.tu-muenchen.de

utilizing this concept have been developed with complexes of Cu, Ru, Ni, Pd, Rh, and Fe to establish the ATRP equilibrium.[4] We recently reported on the exceptional efficiency and versatility of new catalysts based on $[RuCl_2(arene)(PR_3)]$ for promoting ATRP of vinyl monomers.[5] As these complexes were also known to be highly active for olefin metathesis,[6] we then moved to $[RuCl_2(=CHPh)(PCy_3)_2]$ (**1**), the Grubbs' ruthenium benzylidene complex which has had a tremendous impact on this field.[7] Since initial results showed that complex **1** proved to be highly efficient also for ATRP,[5] we expanded our investigations towards the latest catalyst development in this field, that is, NHC-containing ruthenium benzylidene complexes introduced by Herrmann et al.[8]

Results and Discussion

Catalytic investigations: In a first set of experiments, we checked the catalytic activity of ruthenium benzylidenes **1**–**3** with methyl methacrylate (MMA) at 85 °C, with ethyl 2-bromo-2-methylpropanoate as initiator (Table 1). All of the complexes were found to catalyze the polymerization of MMA in high yield and in a fairly well controlled way, although significant differences in their behavior were noticed. Thus, mixed ligand complexes **2** exhibited the lowest activity, whereas little difference was noticed between bis(imidazol-2-ylidene) compounds **3a** (R = Cy) and **3b** (R = *i*Pr); both of them afforded poly(methyl methacrylate) (PMMA) possessing essentially the same features (M_n and M_w/M_n). Complex **1** gave the narrowest molecular weight distribution ($M_w/M_n = 1.28$), although the number-average molecular weight (M_n) was higher than the calculated value (initiation efficiency (f) = 0.6). Broader M_w/M_n values resulted from substitution of one or both PCy_3 by a *N*-heterocyclic carbene. With complexes **3**, M_n values were fairly well controlled by the monomer to the initiator ratio ($f \approx 0.9$). Complex **3a** was also employed in conjunction with polyhalogenated initiators (CCl_4 and CCl_3Br) and tested with $Al(OiPr)_3$ as a co-catalyst,[4a, 9] but without any significant improvements regarding the control of polymerizations (Table 2). As already previously noticed for polyhalogenated initiators,[10, 11] the initiation efficiency factor f was then higher than 1, indicating the generation of additional polymer chains through transfer reactions.[12]

Table 1. Ruthenium-catalyzed polymerization of methyl methacrylate and styrene.

	Methyl methacrylate[a]				Styrene[b]			
	Yield [%]	M_n[c]	M_w/M_n	f[d]	Yield [%]	M_n[c]	M_w/M_n	f[d]
1	95[e]	66000[e]	1.28[e]	0.6[e]	61	29000	1.38	0.8
2b	85	58000	1.35	0.6	48	22000	1.6	0.85
3a	99	42000	1.47	0.95	89	39000	1.53	0.9
3b	90	43000	1.6	0.85	78	36000	1.8	0.85
4	97	49500	1.47	0.8				

[a] $[MMA]_0/[initiator]_0/[Ru]_0 = 800:2:1$ (initiator = ethyl 2-bromo-2-methylpropanoate, $T = 85$ °C, reaction time = 16 h). [b] $[styrene]_0/[initiator]_0/[Ru]_0 = 750:2:1$ (initiator = (1-bromoethyl)benzene, $T = 110$ °C, reaction time = 16 h). [c] Determined by size-exclusion chromatography (SEC) with PMMA and polystyrene calibration, respectively. [d] Initiation efficiency $f = M_{n,theor}/M_{n,exp}$ with $M_{n,theor} = ([monomer]_0/[initiator]_0) \times M_w(monomer) \times$ conversion. [e] See refs. [5a, 8].

Table 2. Polymerization of methyl methacrylate catalyzed by complex **3a** and initiated by polyhalogenated compounds.[a]

Initiator	Co-catalyst[b]	Yield [%]	M_n[c]	M_w/M_n	f[d]
CCl_4	–	98	30500	1.57	1.3
CCl_4	$Al(OiPr)_3$	95	26000	1.45	1.45
CCl_3Br	–	100	42000	1.39	0.95
CCl_3Br	$Al(OiPr)_3$	100	34000	1.42	1.2

[a] $[MMA]_0/[initiator]_0/[Ru]_0 = 800:2:1$ ($T = 85$ °C, reaction time = 16 h). [b] Four equivalents relative to **3a**. [c] Determined by size-exclusion chromatography (SEC) with PMMA calibration. [d] Initiation efficiency $f = M_{n,theor}/M_{n,exp}$ with $M_{n,theor} = ([MMA]_0/[initiator]_0) \times M_w(MMA) \times$ conversion.

The MMA polymerization apparently proceeds by a radical mechanism, as indicated by the inhibiting effect of radical scavengers (galvinoxyl or 1,1-diphenyl-2-picrylhydrazyl (DPPH), five equivalents relative to complexes **1** and **3a**), and by the close similarity of the tacticity of the PMMA thus obtained and that of PMMA radically prepared with azobis(isobutyronitrile) (AIBN) in toluene at 85 °C. Interestingly, the tacticity of PMMA and polystyrene was not affected by the use of chiral complex **2b**. For PMMA, for instance, the tacticity (*rr*:*rm*:*mm* = 59.25:37.15:3.6) was close to that measured for most PMMAs synthesized by ATRP, irrespective of the catalyst ligands.[5a]

Under those conditions, the kinetics were first order in MMA (Figure 1), and the number-average molecular weight (M_n) of PMMA increased linearly with monomer conversion (Figure 2), although they were (slightly) higher than the calculated values assuming that one molecule of initiator generates one living polymer chain. Furthermore, the molecular weight distribution (M_w/M_n) decreased as the polymerization proceeded (Figure 2), indicating that the radicals are long-lived.

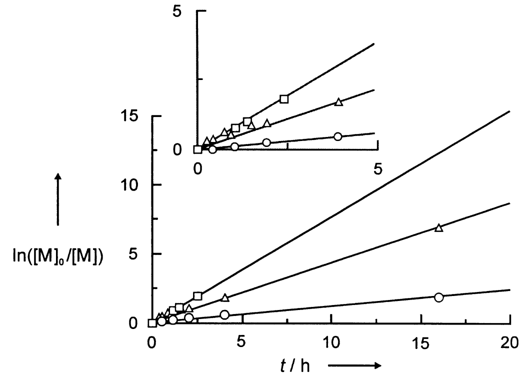


Figure 1. Time dependence of $\ln([M]_0/[M])$ at 85 °C where $[M]_0$ and $[M]$ are the MMA concentration at times 0 and t, respectively. Reaction conditions are the same as in Table 1. Catalysts: **1** (□) $y = -1.5333 \times 10^{-2} + 0.75725x$; $r^2 = 0.999$. **2b** (○) $y = 6.8162 \times 10^{-2} + 0.11581x$; $r^2 = 0.993$. **3a** (△, two superimposed runs), $y = 0.22705 + 0.41747x$; $r^2 = 0.998$.

Mechanistic approach: The complexes used in this paper are extensively employed in olefin metathesis and they have now been shown to catalyze ATRP. This raises a fundamental

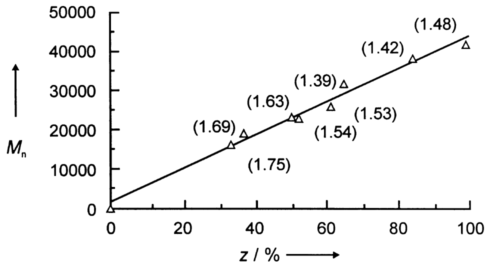
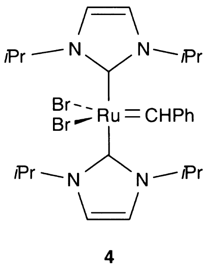


Figure 2. Dependence of the PMMA molecular weight M_n on monomer conversion z ($y = 1739.0 + 423.08x$; $r^2 = 0.982$; two superimposed runs). Reaction conditions are the same as in Table 1 (catalyst = **3a**). (Catalyst **1**, $y = -2012.4 + 666.59x$; $r^2 = 0.986$; catalyst **2b**, $y = 2062.2 + 670.92x$; $r^2 = 0.996$; catalyst **3b**, $y = 1849.0 + 485.07x$; $r^2 = 0.986$).

question: Is this observation merely coincidental, or does it reflect a common requirement of both reactions, which would just be met with ruthenium–benzylidene complexes? The mechanisms of olefin metathesis and ATRP are both well known (even though numerous aspects thereof still need further clarification) and are completely different. However, the recent observation that the Grubbs' catalyst **1** generates persistent radical anions on treatment with π acceptors and a remarkably wide range of dienes and even simple alkenes[13] led us to compare the mechanisms of both reactions catalyzed by **1**–**3**.

Ruthenium–alkylidene complexes **1**–**3** are unsaturated 16-electron species that formally allow carbon–halogen bond activation to form a 17-electron ruthenium(III) intermediate. Our preliminary results summarized hereafter indicate that polymerization occurs through a pathway in which both tricyclohexylphosphane and/or imidazol-2-ylidene ligands remain bound to the metal center:

1) MMA polymerizations clearly demonstrated a significant increase in the catalytic activity of the bis-phosphane complex **1** when compared to the bis(imidazol-2-ylidene) and to the mixed ligand derivatives, **3** and **2**, respectively (Figure 1, **1** ($k_{app} = 21.05 \times 10^{-5}\,s^{-1}$), **2b** ($k_{app} = 3.22 \times 10^{-5}\,s^{-1}$), **3a** ($k_{app} = 11.60 \times 10^{-5}\,s^{-1}$), **3b** ($k_{app} = 8.76 \times 10^{-5}\,s^{-1}$)[14]). An exactly opposite trend was observed in olefin metathesis[3g] in which phosphane dissociation from the metal center was shown to take place.[15] An interesting result came from the comparison of complex **3b** and its dibromo analogue **4**, which were found to be essentially equipotent catalyst precursors both for ATRP and olefin metathesis.[3g] This reactivity pattern appears to be in sharp contrast to that of the parent system **1**, the efficiency of which dropped significantly when the chloride ligands were replaced by bromide or iodide.[15, 16]



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2) Catalytic activity for MMA polymerization was only slightly influenced by an excess of PCy_3 to the reaction medium[17] (Figure 3a), which stands in contrast to olefin metathesis activity with the same catalyst precursor.[3e, 15] Quite the contrary, with complex **2b** the rate of polymerization increased by a factor of three upon addition of five equivalents of PCy_3. These results rule out again a dissociative pathway. An excess of PCy_3 led, however, to some loss of the control of M_n (Figure 3b) and to a significant broadening of the polydispersity (Figure 3c). When five equivalents of PCy_3 were added to **1** and **2b**, M_w/M_n reached 1.5 and 1.85, respectively. The possibility that free phosphanes or *N*-heterocyclic carbenes also act as initiators (or are actually the initiators) in these polymerization reactions has been excluded by control experiments with just the ligand. PPh_3, PCy_3, and 1,3-bis(2,4,6-trimethylphenyl)-2,3-dihydro-1*H*-imidazol-2-ylidene have been tested as potential initiators for the polymerization of methyl methacrylate at 85 °C, and found to be inactive.

3) With the bis(imidazol-2-ylidene) complex **3a** (R = Cy), the plot of ln([M]$_0$/[M]) versus time was linear, whereas with **3b** (R = *i*Pr) the relationship was asymptotic (Figure 4). These results could be rationalized by the relative stability of those ruthenium complexes. The more sterically demanding imidazol-2-ylidenes (R = Cy, 2,4,6-trimethylphenyl) are known to be stronger binders to ruthenium and to form more stable complexes than their isopropyl-substituted counterpart.[3e, 18] The less bulky tetramethyl derivative (**3**, R = Me) could never be isolated.[19]

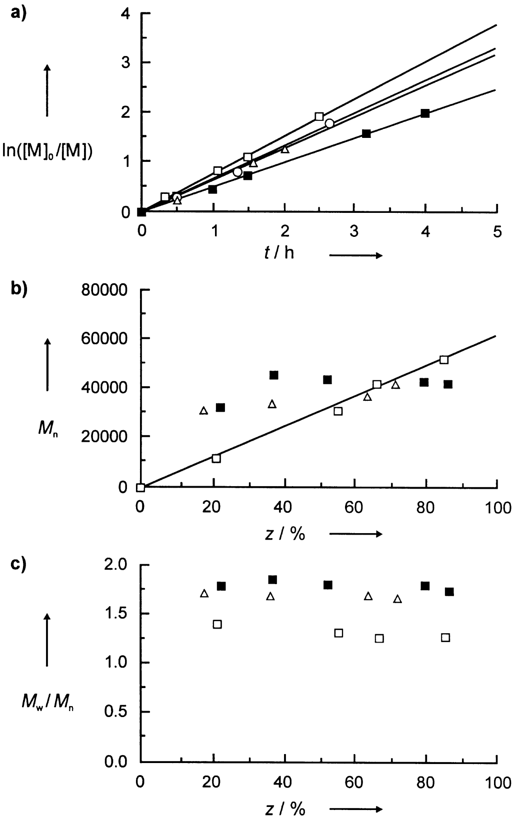

Figure 3. a) Time dependence of ln([M]$_0$/[M]) at 85 °C where [M]$_0$ and [M] are the MMA concentration at times 0 and t, respectively. Reaction conditions are the same as in Table 1. Catalyst systems: **1**, no added PCy_3 (□) ($y = -0.015333 + 0.75725x$; $r^2 = 0.999$); **1** + 2 PCy_3 (○) ($y = -0.032839 + 0.66585x$; $r^2 = 0.997$); **1** + 5 PCy_3 (△) ($y = -0.086701 + 0.65601x$; $r^2 = 0.975$); **1** + 10 PCy_3 (■) ($y = -0.010778 + 0.49681x$; $r^2 = 0.999$). b) Dependence of the PMMA molecular weight M_n and c) of the molecular weight distribution M_w/M_n on monomer conversion z. Catalyst systems: **1**, no added PCy_3 (□); **1** + 5 PCy_3 (△); **1** + 10 PCy_3 (■).

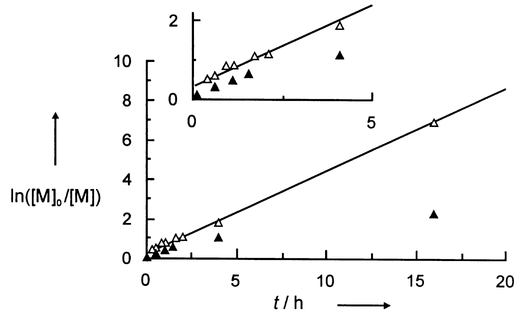

Figure 4. Time dependence of ln([M]$_0$/[M]) at 85 °C where [M]$_0$ and [M] are the MMA concentration at times 0 and t, respectively. Reaction conditions are the same as in Table 1. Catalysts: **3a** (△), $y = 0.22705 + 0.41747x$; $r^2 = 0.998$. **3b** (▲), $y = 0.06830 + 0.31529x$; $r^2 = 0.973$, calculated for the first three hours of polymerization.

The fate of the alkylidene fragment in complexes **1**–**3** remains a matter of debate.[3e, 20] The thermal stability of benzylidene complexes **1**, **2b**, and **3b** was tested at 85 °C, under conditions mimicking polymerization of methyl methacrylate.[21] As monitored by ^{1}H NMR spectroscopy, complete disappearance of the benzylidene fragment of **2b** was observed within 20 min, whereas **1** showed only 55 % decomposition over the same period of time (88 % decomposition of complex **3b**).[22] A typical reaction profile for this process appears in Figure 5a. These results indicate that ATRP is mediated by ruthenium species bereft of the benzylidene moiety. However, no induction periods were observed in the kinetics (Figure 1), and it is therefore more likely that both complexes **1**–**3** and their decomposition products catalyze ATRP, and probably at different rates. Thus, the observation of nonlinear rate constants presented in Figure 4 for complex **3b** could also be seen as supporting this claim.

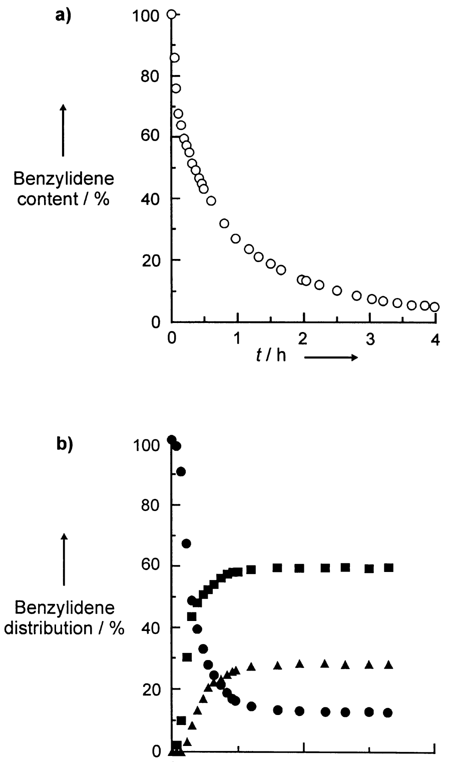

Figure 5. a) Time dependence of the benzylidene content (○) and b) of the benzylidene distribution by heating complex **1** at 85 °C in the presence of ethyl 2-bromo-2-methylpropanoate:[21] [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] (●, **1**), [RuBrCl(=CHPh)(PCy$_3$)$_2$] (■), and [RuBr$_2$(=CHPh)(PCy$_3$)$_2$] (▲).

Further interesting information stems from the rate studies of using complexes **1** and **2b** in the presence of excess PCy$_3$. Addition of PCy$_3$ slightly slowed down the polymerization rate (Figure 3a). Thus, the addition of ten equivalents of PCy$_3$ afforded a polymerization rate constant of 13.8×10^{-5} s^{-1}. Since it is well known that additional PCy$_3$ also extends the longevity of the catalysts,[20] this result might most likely reflect polymerization mediated by complex **1**. When no PCy$_3$ was added, the rate constant increased to 21.05×10^{-5} s^{-1}, which might reflect mediation by the decomposed species. Furthermore, addition of PCy$_3$ also resulted in a nonlinear relationship of M_n versus conversion (Figure 3b) and a quite broad polymer distribution (Figure 3c), revealing a redox-initiated free-radical polymerization. This could tentatively be rationalized by the fact that the ruthenium–benzylidene complexes **1**–**3** mediate (to some extent) olefin polymerization throught a redox-initiated free-radical process and that the ruthenium species bereft of the benzylidene fragment are the active ATRP catalysts.

In the early stages of the decomposition reaction of the ruthenium–benzylidene complexes, halogen exchange took place between [RuCl$_2$(=CHPh)L$_2$] complexes **1** and **3b** (L = PCy$_3$ or NHC), the initiator (ethyl 2-bromo-2-methylpropanoate) and/or the carbon–halogen terminii of the dormant species (Figure 5b). These halogen exchanges yielded first new complexes, tentatively identified as [RuClBr(=CHPh)L$_2$], which were then converted into [RuBr$_2$(=CHPh)L$_2$], unambiguously identified by comparison with authentic samples.[23] No evidence so far (^{1}H and ^{13}C NMR spectroscopy) substantiated the intermediacy of [Ru=C(Me)CO$_2$Me] or [Ru=CH$_2$] species, potentially resulting from a metathetical exchange between the benzylidene fragment of **1** or **3b** and methyl methacrylate. Ruthenium ester carbene complexes, [Ru=C(Me)CO$_2$R], are known to be highly unstable,[25] and it is possible that this species forms and then quickly decomposes. In addition, while it is well known that complex **1** is inert towards methacrylates, related *N*-heterocyclic carbene complexes **2** have been recently shown to react with these substrates to some extent.[26] The observed thermolytic half-lives[22] approximate the relative reactivity of the complexes with methacrylates and help to support this claim. Further proof of this possible reaction pathway is needed. Likewise, the real catalytic species remains unknown so far, and a more detailed investigation of these processes is presently under way.

Catalysts **1**–**3** also permit a satisfactory control of styrene polymerization. This was not possible with the early ruthenium-based catalysts till the recent introduction of [RuCl$_2$(p-cymene)(PR$_3$)][5] and [RuCl(Ind)(PPh$_3$)$_2$] (Ind = indenyl).[27] With complex **1** (Table 1), a smooth polymerization of styrene took place. The conversion reached 61 % in 16 h, with a molecular weight distribution near 1.4. M_w/M_n were however broader for polystyrenes obtained using ruthenium *N*-heterocyclic carbene complexes **2** and **3** ($M_w/M_n = 1.55$–1.8). It should be noted that vinyl acetate (a substrate known to be very reluctant to undergo ATRP[28]) polymerized in moderate yields at 140 °C, although in an uncontrolled way (Table 3). Likewise, the polymerization of *n*-butyl acrylate (Table 3) was not controlled, as with all other ruthenium complexes reported so far, except for $[RuCl_2(p\text{-cymene})(PiPr_3)]$[29] and $[RuCl(Cp^*)(PAr_3)_2]$.[30] With both monomers, polymerization is more likely a redox-initiated free-radical process, as indicated by the kinetics and the evolution of molecular weights with conversion (Figure 6).[28a,b]

Table 3. Ruthenium-catalyzed polymerization of *n*-butyl acrylate and vinyl acetate.

	n-Butyl acrylate[a]				Vinyl acetate[b]			
	Yield [%]	M_n[c]	M_w/M_n	*f*[d]	Yield [%]	M_n[c]	M_w/M_n	*f*[d]
1[e]	82	43500	1.75	0.7	20	13000	1.8	0.6
2b	94	90000	2.9	0.4				
3a	100	56000	2.45	0.7				
3b[f]	100	54000	2.1	0.7	26	12500	2.0	0.85

[a] [*n*-butyl acrylate]$_0$/[initiator]$_0$/[Ru]$_0$ = 600:2:1 (initiator = ethyl 2-bromopropanoate, T = 85 °C, reaction time, 16 h). [b] [vinyl acetate]$_0$:[initiator]$_0$:[Ru]$_0$ = 930:2:1 (initiator, ethyl 2-bromo-2-methylpropanoate, T = 140 °C; reaction time = 3 days). [c] Determined by size-exclusion chromatography (SEC) with PMMA calibration. [d] Initiation efficiency $f = M_{n,theor}/M_{n,exp}$ with $M_{n,theor}$ = ([monomer]$_0$/[initiator]$_0$) × M_w(monomer) × conversion. [e] Reaction time = 1 day (7 days), yield = 12% (32%), M_n = 12000 (18000), M_w/M_n = 2.05 (1.65). [f] Reaction time = 1 day (7 days), yield = 20% (29%), M_n = 12000 (17000), M_w/M_n = 2.05 (1.8).

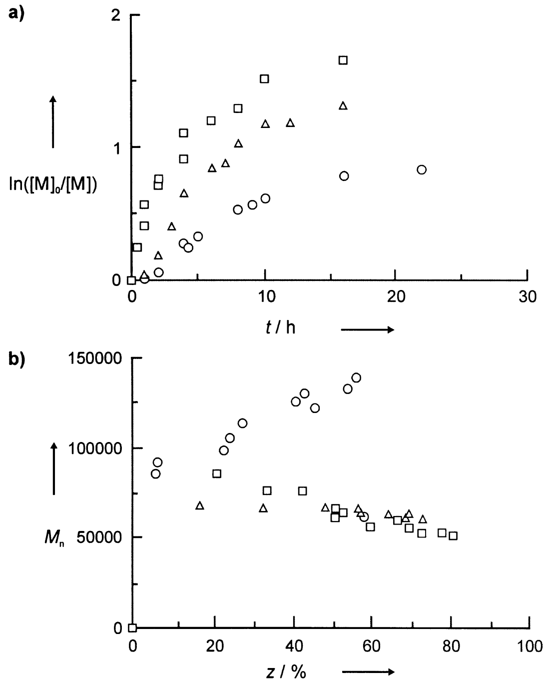

Figure 6. a) Time dependence of ln([M]$_0$/[M]) at 65 °C where [M]$_0$ and [M] are the *n*-butyl acrylate concentration at times 0 and *t*, respectively, and b) dependence of the poly(*n*-butyl acrylate) molecular weight M_n on monomer conversion *z* (two superimposed runs). Catalysts: **1** (□), **2b** (○), and **3a** (△). Reaction conditions: [*n*-butyl acrylate]$_0$/[initiator]$_0$/[Ru]$_0$ = 1200:4:1 (initiator, ethyl 2-bromopropanoate). M_n were determined by size-exclusion chromatography (SEC) with PMMA calibration.

Conclusion

We have demonstrated that ruthenium benzylidenes with *N*-heterocyclic carbene ligands are efficient catalysts for the controlled radical polymerization of methyl methacrylate and styrene. Since these complexes also exhibit excellent performance in olefin metathesis, there is clearly a great deal of promise in elucidating the nature and the reactivity of those intermediate species, and for further improvements of *N*-heterocyclic carbene-containing catalysts for both reactions.

Experimental Section

General: All reagents and solvents were dried, distilled, and stored under nitrogen at −20 °C with conventional methods.[31] Grubbs catalyst **1** was used as received (Strem). Ruthenium complexes **2**–**4** were synthesized and purified according to the literature.[3a,b,d]

Polymerization of MMA: The ruthenium complex (0.0117 mmol) was placed in a glass tube containing a bar magnet and capped by a three-way stopcock. The reactor was purged of air (three vacuum–nitrogen cycles) before methyl methacrylate (1 mL, 9.35 mmol), and the initiator (ethyl 2-bromo-2-methylpropanoate 0.1 M in toluene, 0.234 mL) were added. All liquids were handled with dried syringes under nitrogen. The mixture was heated in a thermostated oil bath for 16 h at 85 °C and, after cooling, dissolved in THF and the product precipitated in heptane. The polymer was filtered off and dried overnight at 80 °C under vacuum.

Styrene, *n*-butyl acrylate, and vinyl acetate were polymerized according to the same procedure. In all experiments, 1 mL of monomer was used (for further information on the initiator, the temperature and the reaction time, see Tables 1–3). In two cases (Table 2), aluminum isopropoxide (Acros, 0.095 M in dry toluene, 0.5 mL) was added to the reaction mixture.

Characterization: The molecular weight distribution was analyzed by size-exclusion chromatography (SEC) in THF at 40 °C by using a Hewlett–Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector. PMMA and polystyrene standards (Polymer Laboratories) were used for calibration. Before SEC analysis, the polymer was purified by passing solutions through an Al_2O_3-filled column. ^1H NMR spectra were recorded at room temperature in $CDCl_3$ with TMS as internal reference by using a Brucker AM400 apparatus.

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[17] Complex **1**: no added PCy$_3$, $z_{(2h)} = 78\,\%$, $k_{app} = 21.05 \times 10^{-5}\,s^{-1}$; 2 equiv PCy$_3$, $z_{(2h)} = 73\,\%$, $k_{app} = 18.5 \times 10^{-5}\,s^{-1}$; 5 equiv PCy$_3$, $z_{(2h)} = 71\,\%$, $k_{app} = 18.2 \times 10^{-5}\,s^{-1}$; 10 equiv PCy$_3$, $z_{(2h)} = 63\,\%$, $k_{app} = 13.8 \times 10^{-5}\,s^{-1}$.

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[21] Ruthenium complex (0.0117 mmol), ethyl 2-bromo-2-methylpropanoate (0.0204 mmol), methyl methacrylate (0.312 mmol), anthracene (internal standard, 0.0056 mmol), [D$_8$]toluene (1 mL).

[22] Thermolytic half-lives: **1**: 16.5 min, **2b**: 5 min, **3b**: 7.5 min.

[23] After about 40 min, the remaining benzylidene fragment of complex **1** was distributed amongst [RuBr$_2$(=CHPh)(PCy$_3$)$_2$] (28 %), [RuClBr(=CHPh)(PCy$_3$)$_2$] (59 %), and **1** (13 %) (Figure 5b). With complex **3b**, the dibromo complex **4** was the predominant species in solution (up to 70 %) compared to the mixed bromo–chloro (27 %), and to the starting dichloro (**3b**) (3 %) derivatives. It is thus tempting to correlate the preference for bromo–ruthenium complexes to the observation that most of the PMMA chains are capped by a Cl atom.[10, 24]

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[29] [RuCl$_2$(*p*-cymene)(P*i*Pr$_3$)] was the first ruthenium-based catalyst to afford a rather controlled polymerization of *n*-butyl acrylate ($M_w/M_n = 1.4$).[5]

[30] [RuCl(Cp*)(PAr$_3$)$_2$] (Ar = C$_6$H$_5$, *p*-CH$_3$OC$_6$H$_4$, and *p*-CF$_3$C$_6$H$_4$) are so far the best ruthenium-based catalysts for the controlled radical polymerization of acrylates. Very narrow molecular weight distributions were obtained ($M_w/M_n = 1.1–1.2$).[27b] See also: F. Simal, PhD Thesis, University of Liège, (Belgium) **2000**.

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