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Controlled Radical Polymerization Mediated by Cationic Arene Ruthenium Complexes

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Summary

Cationic allenylidene ruthenium complexes, $[Ru{=}C{=}C{=}CPh_2(L)(p\text{-cymene})]PF_6$ (L = PCy_3, 1,3-dimesityl-4,5-dihyroimidazol-2-ylidene) are implemented as versatile catalyst for the controlled atom transfer radical polymerization of vinylmonomers and deliver high molecular weight polymers with a quite narrow molecular weight distribution. Improvements on the activity can be made by adding additives or transforming the allenylidene entity into a corresponding Fischer carbene.

Introduction

Transition metal complexes are widely used in synthetic organic chemistry owing to their ability for precise control over a wide range of reactions [1]. In particular, some transition complexes are known to promote the activation of carbon-halogen bonds to generate radical species which can be involved in subsequent addition reactions [2]. Among these reactions is situated the so-called atom transfer radical polymerization (ATRP). ATRP is based on a dynamic equilibrium between a low concentration of active propagating radicals and a large amount of dormant species. This equilibrium is established through the reversible transition metal-catalyzed homolytic cleavage of a covalent carbon-halogen in the dormant species and an accompanying one-electron oxidation of the transition metal (Scheme 1).

$$R{-}X + L_nMt^{(n)} \rightleftharpoons R^{\bullet} + L_nM_t^{(n+1)}X$$

Dormant species

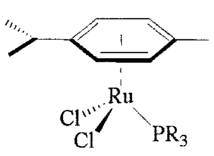
Active species

Scheme 1: Mechanism of Atom Transfer Radical Polymerization.

This equilibrium is prominently shifted toward the side of the dormant species. The concentration of propagating radicals remains low throughout the polymerization process which allows not only to synthesize macromolecules with predetermined molecular weights and low polydispersities, but also the preparation of novel, functionalized copolymers (block, graft, gradient, etc.) [3]. The element ruthenium has played a prominent role in the discovery of ATRP [4].

Especially, the arene ruthenium system (**1**) has proven to be an efficient and versatile catalyst for promoting the ATRP of vinylmonomers without co-catalysts activation [5]. In the recent literature there has been some turmoil because it was demonstrated that ruthenium benzylidene complexes, $RuCl_2(=CHPh)LPCy_3$ (L = PCy_3, N-heterocyclic carbene), which acts as one of the standards in olefin metathesis such as Ring Opening Metathesis (ROMP), Ring Closing Metathesis (RCM) and cross metathesis, were also extremely active for the ATRP of some activated vinyl monomers [6]. When complex **1** is activated with trimethylsilyldiazo methane, for the generation of a carbene species, this complex is useable for ROMP of cyclic olefins [7]. Moreover, when the phosphine ligand is changed by a N-heterocyclic carbene, this complex is capable to perform ROMP of cyclooctene via an activation with visible light [8]. During the last years our group became more and more interested to broaden the horizon of highly active half-sandwich (arene)-ruthenium catalysts that are dual active in ROMP and ATRP reactions [9].

We now report about the versatile allenylidene Ru-complexes (**2-3**) that can polymerize norbornene, cyclooctene and cyclopentene with a very low catalyst loading [10]. These cationic 18-electron allenylidene ruthenium complexes, which are easily available from $RuCl_2(L)(p\text{-cymene})$, 1,1-diphenyl-2-propyn-1-ol and sodium salts like $NaPF_6$, have proven to be excellent catalyst precursors for ring closing olefin metathesis [11]. When these systems operate under ATRP conditions, they show also a moderate activity for the controlled radical polymerization of MMA, styrene and acrylates. The activity of these complexes can be increased by adding appropriate additives such as $n\text{-}Bu_2NH$.



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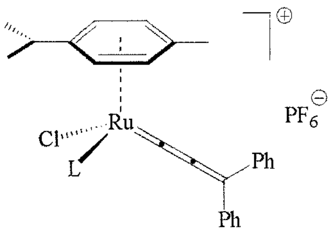

2 L = PCy_3
3 L = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene

Experimental

Materials

All monomers (Aldrich) were distilled from CaH_2 and stored under nitrogen at –20 °C. Ethyl 2-bromo-2-methylpropionate, (1-bromoethyl)benzene, ethyl 2-bromopropionate and carbontetrachloride were used as received (Aldrich). Catalysts **2** was prepared according to literature procedures [12]. Catalyst **3** was prepared as follows: A 100 ml Schlenck flask equipped with a stirring bar was charged with 1,3-dimesityl-4,5-dihydroimidazolium tetrafluoroborate (2 g, 5 mmol) and dry THF (15 ml) under an argon atmosphere. To this suspension 5 ml (1 M in diethylether) of potassium *tert*-butoxide was slowly added to the stirred solution at room temperature which resulted in the dissolving of the salt. This mixture was stirred for 30 min at room temperature and then transferred to another Schlenk flask containing 30 ml of dry benzene. Complex **2** was slowly added (4.25 g, 4.8 mmol) and the mixture was heated at 70 °C during 1 h. After the reaction, the volatiles were removed under vacuum, and the residue was washed with anhydrous methanol (3x10 ml) to give a violet microcrystalline solid in 73% yield. ^{1}H-NMR (300 MHz, C_6D_6, 25°C) $\delta = 7.72$ (m, 4H), 7.42 (m, 2H), 7.31 (m, 4H), 7.28-6.99 (m, 4H), 6.56 (dm, 1H, $J = 6$ Hz), 6.36 (dm, 1H, $J = 6.3$ Hz), 5.68 (dm, 1H, $J = 6$ Hz), 5.58 (dm, 1H, $J = 6.5$ Hz), 3.81 (s, 4H), 2.73 (hept, 1H), 2.32-1.94 (br, 18H), 2.19 (s, 3H), 1.14 (m, 6H). ^{13}C-NMR (75 MHz, C_6D_6, 25°C) $\delta = 278.12$ (C_α), 185.52 (C_β), 165.54 (C_γ), 144.54, 141.88, 140.5, 139.0, 138.7, 137.0, 135.8, 133.9, 132.1, 130.25, 129.8, 129.0, 128.9, 128.4, 127.6, 125.5, 22.6, 21.0, 21.2, 19.5, 19.3, 18.5, 17.5. ^{31}P-NMR (C_6D_6, 25°C) $\delta = -140.9$ (s).Anal. Calcd for $C_{44}H_{50}ClF_6N_2PRu$: C 59.49, H 5.67, N 3.15. Found: C 59.63, H 5.90, N 3.30.

Instruments

Gel Permeation chromatography (GPC) analysis was performed on a Shimadzu Class-VP™ instrument using three PL columns (PSS SDV: 30 cm, ∅ = 8 mm, 10^3, 10^4, 10^5 Å) with chloroform as the eluent. Calibration was conducted with PMMA and PS standards.

Polymerization

A typical ATRP experiment is as followed: Ruthenium complex (0.0117 mmol) was transferred in a glass vessel which is continuously purged with argon. Then a magnetic stirrer, the monomer (9.35 mmol) and 465 μl of an initiator solution (0.05 M in toluene) were subsequently added. The mixtures were heated in a thermostated oil bath for 16 h at 85 °C for methacrylates and acrylates and 110°C for styrene. After cooling, the mixtures were diluted in chloroform and after filtration through a short silica gel columns, the polymers were precipitated into vigorously stirred *n*-octane (acrylates, methacrylates) or methanol (styrene). The white, tacky polymers obtained in this way were filtrated and dried overnight under vacuum at 40 °C.

Results and discussion

Common vinyl monomers such as styrene (St), methylmethacrylate (MMA), methylacrylate (MA) and isobutylmethacrylate (IBMA) were chosen as model substrate for the catalyst screening on ATRP and ethyl 2-bromo-2-methylpropionate, methyl 2-bromopropionate and (1-bromoethyl)benzene were chosen as initiator for the polymerization of methacrylates, methylacrylate and styrene respectively.

From the results summarized in Table 1 it appears that moderate to good yields are obtained for the polymerization of MA (80%), BA (69%), styrene (65%), IBMA (40%) and MMA (44%) with catalyst **3** while the activity is much lower with system **2** (all < 40%). The polymerization of MMA and styrene mediated with both catalysts is well-controlled as indicated by the narrow molecular weight distribution for MMA and styrene (M_w/M_n = 1.18-1.40) and the high initiation efficiency (f > 0.7 for most monomers). For the monomers MA and IBMA the molecular weight distribution is somewhat broader (M_w/M_n = 1.33-1.56) and the initiation process is less efficient (f = 0.62 and 0.14). The polymerization of MMA and St can also be initiated by CCl_4 which causes a slight increase in activity for both catalytic systems. However, as more initiated species are generated the initiation efficiency was increased (f > 0.8) but this lead also to more bimolecular combinations of radicals especially in the beginning of the reaction which is indicated by a broadening of the polydispersity (e.g. 1.44 versus 1.4 and 1.50 versus 1.18 for St mediated by **2** and **3**). The ATRP of styrene initiated with (1-bromoethyl)benzene and the different catalysts was monitored at 110°C. The semi-logarithmic plot of $\ln([M]_0/[M])$ vs. time was linear, with apparent rate coefficient (k_{app}) of $5.14.10^{-6}$ s^{-1} for **2** and $1.77.10^{-5}$ s^{-1} for **3** indicating that the radical concentration remains constant throughout the polymerization (Fig. 1). Transfer reactions can for a great part excluded as supported by the linearity of the plot of M_n versus conversion (Fig. 2).

Table 1: ATRP of vinylmonomers using catalysts **2** and **3**.[a]

Monomer	Cat.	Yield (%)	$M_n(x10^3)$[c]	M_w/M_n[c]	f[d]
MMA	**2**	14	10.0	1.35	0.56
MMA[b]	**2**	36	17.8	1.39	0.81
IBMA	**2**	17	13.4	1.33	0.72
MA	**2**	40	19.8	1.37	0.69
BA	**2**	33	24.9	1.39	0.67
St	**2**	27	15.6	1.40	0.72
St[b]	**2**	63	32.5	1.44	0.81
MMA	**3**	44	46.8	1.46	0.38
MMA[b]	**3**	47	25.0	1.40	0.75
IBMA	**3**	40	167	1.47	0.14
MA	**3**	80	44.5	1.56	0.62
BA	**3**	69	47.7	1.42	0.74
St	**3**	65	34.6	1.18	0.78
St[b]	**3**	70	39.6	1.50	0.74

[a] General conditions: [Monomer]:[Ru]:[Ininiator] = 800: 1: 2, Solvent: 1 ml toluene, 85°C for acrylates and methacrylates, 110°C for styrene, 17 h.[b] initiator = CCl_4 [c] Determined with Gel permeation Chromatography using PS and PMMA standards. [d] Initiator efficiency $f = M_{n,theor}/M_{n,exp.}$ with $M_{n,theor.}$ = $([Monomer]_0/[Initiator]_0)$ x $M_{w,monomer}$ x conversion.

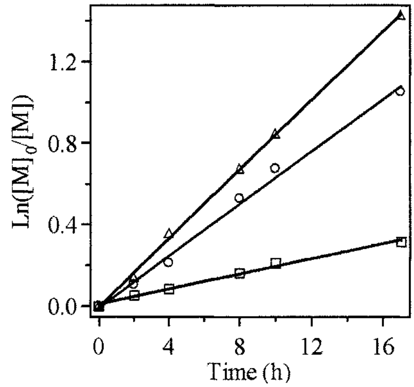

Figure 1: Time dependence of ln($[St]_0$/[St]) at 110°C, where $[St]_0$ and [St] are the St concentrations at times 0 and t. $[St]_0$ = 3.74 M. (□ **2** y = 0.0185x+0.0105, r^2 = 0.993, ○ **3** y = 0.0639x-0.0086, r^2 = 0.994, Δ **3**+ethylvinyl ether y = 0.0844x-0.0036, r^2 = 0.999.)

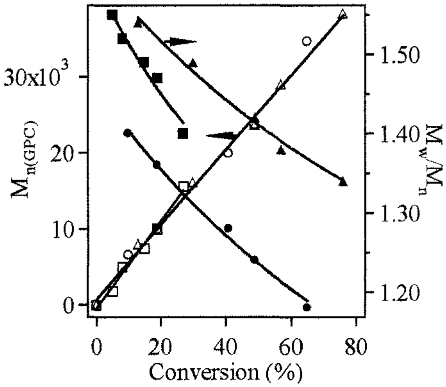

Figure 2: Dependence of the polystyrene molecular weight (□ **2**, ○ **3**,Δ **3**+vinylether) and polydispersity (■ **2**, ● **3**, ▲ **3**+ethylvinylether) on the monomer conversion at 110 °C.

The polymerizations of both MMA and styrene were completely inhibited when 5 eq. of a radical scavenger (e.g. galvinoxyl) was added to the reaction mixture which is in agreement with the radical nature of ATRP. Furthermore, the living character was confirmed by adding a second shot of monomer to the reaction mixture (100 equivalents monomer) which causes a slight increase in polydispersity (Figures 3 and 4).

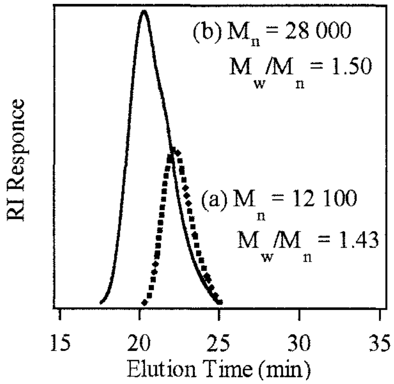

Figure 3: GPC curves of PMMA after a first feed (dashed line) and after a second feed of MMA (solid line). ([MMA]:[In]:[Ru] = 100:2:1)

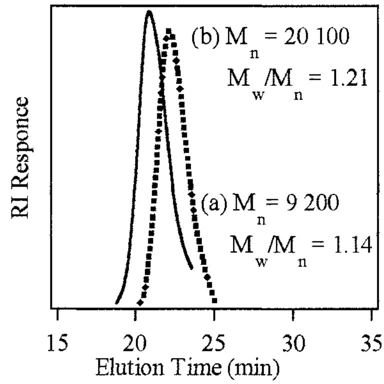

Figure 4: GPC curves of PS after a first feed (dashed line) and after a second feed of Styrene (solid line). ([St]:[In]:[Ru] = 100:2:1)

Recently it was shown by the group of Sawamoto that adding different amines to Ru-catalysed ATRP reactions can dramatically improve the polymerization rate which is also confirmed by our observations (Table 2, 90 and 100% for MMA and 35 and 85%

for styrene with systems 2 and **3**) [13]. The molecular weight distribution is somewhat broader than in the absence of the amine (1.45 versus 1.35 for MMA and 1.54 versus 1.18) and higher molecular weights are obtained than theoretical predicted ($f < 0.7$). However, the exact role of the amine in the ATRP process is not unambiguously clear and demands further experiments.

Since these complexes are cationic species a few experiments were performed in aqueous media. For both catalytic systems, an advantageous effect on the activity was noticed which was very pronounced for the polymerization of styrene where the conversion increased from 27 to 61% with catalysts **2** and from 65 to 80% with catalyst **3**. Unfortunately, this increase in polymer yields is also coupled with a corresponding increase in polydispersity (e.g. 1.58 versus 1.18 with **3**) and a lost of initiator efficiency (0.57 versus 0.78 with **3**).

Table 2: ATRP of MMA and styrene using catalysts **2** and **3** in combination with different additives.[a]

Monomer	Cat.	Additive	Yield (%)	M_n(x10³)[e]	M_w/M_n[e]	f[f]
MMA	**2**	$(n\text{-}Bu)_2NH$[b]	90	51.9	1.45	0.69
	2	H_2O[c]	27	92.7	1.78	0.12
	3	$(n\text{-}Bu)_2NH$[b]	100	60.0	1.59	0.67
	3	H_2O[c]	48	30.6	1.54	0.63
	3	CH_2=CHOEt[d]	72	37.7	1.53	0.76
Styrene	**2**	$(n\text{-}Bu)_2NH$[b]	35	40.4	1.53	0.36
	2	H_2O[c]	61	63.6	1.60	0.40
	3	$(n\text{-}Bu)_2NH$[b]	85	51.8	1.54	0.69
	3	H_2O[c]	80	59.0	1.58	0.57
	3	CH_2=CHOEt[d]	76	42.3	1.34	0.75

[a] General conditions: [Monomer]:[Ru]:[Ininiator] = 800: 1: 2, Solvent: 1 ml toluene, 85°C for acrylates and methacrylates, 110°C for styrene, 17 h. [b] [Ru]:[(n-Bu)$_2$NH] = 1:4. [c] water: 38 v/v %. [d] Fischer carbene prepared *in situ* 0.0117 mmol catalyst and 0.117 mmol ethylvinylether have been reacting for 30 min. before monomer and initiator were added. [e] Determined with Gel permeation Chromatography using PS and PMMA standards. [f] Initiator efficiency $f = M_{n,\,theor}/M_{n,\,exp}$ with $M_{n,\,theor} = ([Monomer]_0/[Initiator]_0) \times M_{w,monomer} \times$ conversion

In a last part of this ATRP investigation, the allenylidene moiety in complex **3** was readily transformed in a ethoxy Fischer carbene by treating it with ethylvinylether. It was already demonstrated that these alkoxy-carbene can be successfully introduced in ATRP and combine high activity with a good control [14]. The polymerization reaction was dramatically accelerated as the apparent rate constant for the ATRP of styrene with **3** is $2.34.10^{-5}$ s^{-1} which is twice the value as with the unmodified complex. Very high yields are obtained for MMA (72%) and styrene (76%) while keeping a good control over the polymerization (Fig. 1 and 2).

Conclusion

We have demonstrated that complexes **2** and **3** posses a good activity toward the ATRP or vinyl monomers. These complexes give access to PMMA and PS with high molecular weights and a narrow polydispersity. These cationic species are able to perform ATRP in aqueous media. The catalytic activity can be dramatically improved by adding *n*-Bu_2NH to the reaction mixture or transforming the allenylidene moiety into an ethoxy Fischer carbene with maintaining a quite good control.

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10. Unpublished results. The ROMP of cyclooctene can be performed with complexes **2** and **3** (Mon/cat = 10000) at room temperature and gave yields of 47 % (M_n = 10x10^5, M_w/M_n = 2.1) and 90% (M_n = 20x10^5, M_w/M_n = 1.9) after 60 min while quantitative yields were reached after 10' at 85°C. Also the less strained cyclopentene can be converted at 85°C and after 17h conversions of 38 % (M_n = 1.98x10^5, M_w/M_n = 2.5) and 75 % (M_n = 2.61x10^5, M_w/M_n = 2.4) were reached (Mon/cat. = 4000).
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