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Atom Transfer Radical Polymerization of vinyl monomers mediated by a new class of neutral and cationic ruthenium alkylidene catalysts containing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and a Schiff base ligand

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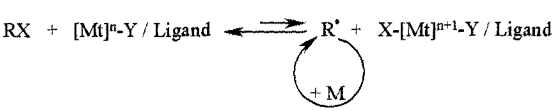
Summary

In this study we examine the Atom Transfer Radical Polymerization (ATRP) of vinyl monomers mediated by a new class of ruthenium alkylidene catalysts containing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and a Schiff base ligand. A controlled radical polymerization can also be achieved with the corresponding cationic complexes using both toluene and a water/toluene mixture as solvent. Our results point out that with these cationic complexes the solvent is crucial for the activity and controllability of the metal-catalysed polymerization. In aqueous/organic biphasic conditions these cationic systems are active in the radical polymerization of hydrophobic monomers such as methyl methacrylate, methyl acrylate and styrene and polymers with controlled molecular weights and narrow molecular weight distributions are obtained.

Introduction

Recent years have witnessed spectacular advances in controlling radical polymerizations via various methods, most of which employ a common concept for controlling the polymerization. This common strategy is based on a lowering of the instantaneous concentration of growing radical species by introduction of a dormant species that exists predominantly over, and in fast equilibrium with, the growth-active radical species [1]. One of the most successful systems is Atom Transfer Radical Polymerization (ATRP), first reported by Sawamoto et al.[2] and Matyjaszewski et al.[3] in 1995. This method owes such controlled formation of radical species to reversible and homolytic cleavage of the dormant carbon-halogen bond through one-electron oxidation of the metal center (Scheme 1)[1].



Scheme 1: Schematic representation of the Atom Transfer Radical Polymerization (ATRP) process.

Recently, we succeeded in synthesizing and characterizing the new class of ruthenium-based catalysts **1.a-f** (figure 1)[4].

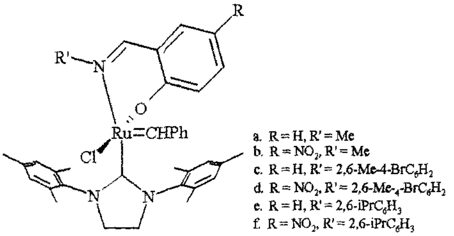


Figure 1: Depicture of the neutral ruthenium alkylidene complexes **1.a-f**.

In this study the controlled radical polymerization of some representative monomers is examined by using by a new class of neutral and cationic ruthenium alkylidene catalysts containing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and a Schiff base ligand in conjunction with an organic halide initiator R-X.

Experimental

General

All reactions and manipulations were performed under an argon atmosphere by using conventional Schlenck-tube techniques. All reagents and solvents used were purchased from Aldrich Chemical Co.. All reagents and solvents were dried, distilled and stored under nitrogen at – 20 °C with conventional methods. ATRP of methacrylates (methyl methacrylate: MMA, isobutyl methacrylate: IBMA), acrylates (methyl acrylate: MA, butyl acrylate: BA) and styrene (St) was carried out with respectively ethyl 2-methyl-2-bromopropionate, methyl 2-bromopropionate and (1-bromoethyl)benzene as initiator. The catalytic systems **1.a-f** were prepared using well-established procedures and were fully characterized by Raman, IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis [4]. The cationic catalytic systems **2.a-f** were prepared in situ by adding 1 equivalent of silver tetrafluoroborate to catalysts **1.a-f**. The polymerizations were carried out under argon atmosphere in sealed glass vials. For the neutral alkylidene ruthenium complexes **1.a-f** a typical ATRP experiment is given below: 0.0117 mmol of catalyst was placed in a glass tube (in which the air was expelled by three vacuum-nitrogen cycles) containing a magnet bar and capped by a three-way stopcock. Then the monomer and initiator were added so that the molar ratios [catalyst]/[initiator]/[monomer] were 1/2/800. All liquids were handled under argon with dried syringes. The reaction mixture was then heated for different time periods at the reaction temperature that was 85°C for the acrylates and methacrylates and 110 °C for St. After cooling, it was diluted in THF and poured in 50 ml n-heptane (for the acrylates, methacrylates) or 50 ml methanol (for styrene) under vigorous stirring. The precipitated polymer was filtered and dried in vacuum overnight. For the polymerization reactions with the cationic ruthenium alkylidene complexes **2.a-f**, the same procedure was followed with this difference that the appropriate solvent was added before heating the reaction mixture. For the polymerizations in toluene, the monomer, the initiator and the catalyst were dissolved in a small amount of toluene so that the monomer/toluene ratio was 1/1 v/v. For the suspension polymerization in water/toluene mixtures, the monomer, the initiator and the catalyst were dissolved in a small amount of toluene, and distilled water was added to the organic solution so that monomer/toluene ratio was 1/3.5 v/v and the water/organic phase ratio 1/1 v/v.

Measurements

The number- and weight-average (M_n and M_w) and polydispersity index (= PDI = M_w/M_n) of the polymers were determined by gel permeation chromatography ($CHCl_3$, 25°C) using polyMMA (for the polyacrylates and polymethacrylates) or polystyrene (for polystyrene) standards. The GPC instrument used is a Shimadzu CLASS-VP^{TM} system equipped with a series of 3 PL gel columns (PSS SDV 30 cm, ∅ = 8 mm, 10^3, 10^4, 10^5 O). Range MW's PS standards: 3250-710000 Dalton. Range MW's polyMMA standards: 2220-772000 Dalton.

Results and discussion

Firstly, we checked the ATRP activity of ruthenium benzylidenes **1.a-f** for some representative monomers. The yields [%] and characteristics of the formed polymers are presented in tables 1 and 2, respectively. Whereas all the catalytic complexes were able to convert styrene (yields varying from 8% for the lowest performing system **1.a** to 75% for the most active system **1.d**), only the complexes **1.c** and **1.d** could polymerize acrylates and methacrylates. It is also noteworthy that the most active systems yield polymers with the narrowest molecular weight distributions. For example, the best system **1.d** reaches conversions of 24 %, 75 % and 27 % for MA, St and MMA generating polymers with polydispersities of 1.21, 1.25 and 1.18, respectively, whereas the less performing system **1.e**, yields the respective polymers in 12% (PDI = 1.39), 43 % (PDI = 1.44) and 11 % (PDI = 1.34). Moreover, it is clear from both the initiator efficiencies (f_i's) and the PDI's of the formed polymers that the control over the radical polymerization process increases in proportion to the activity of the systems. For the most performing ruthenium alkylidene complex **1.d**, the monomer conversion and the number average molecular weight (M_n) were followed in function of time. The plot of $\ln([M_0]/[M_t]$ versus time is linear (figure 2), indicating first-order kinetics. Hence, the number of active species is constant throughout the course of the reaction. This observation together with the linear evolution of molecular weight with conversion (figure 3) indicates that initiation is fast and that the contribution of chain breaking, transfer and termination reactions during the course of the polymerization is negligible; thus, the process is indeed controlled.

	1.a	1.b	1.c	1.d	1.e	1.f
MMA	<5	6	24	27	11	15
IBMA	<5	<5	14	20	7	10
MA	<5	<5	10	24	12	13
BA	<5	<5	12	15	<5	9
St	8	13	67	75	43	51

Table 1: Yield [%] for the ATRP of some representative vinyl monomers catalysed by **1.a-f** (MMA: methyl methacrylate, IBMA: isobutyl methacrylate, MA: methyl acrylate, BA: butyl acrylate, St: styrene).

		M_n(x 10^3)	PDI	f_i
1.c	MMA	14.8	1.23	0.65
	MA	5	1.28	0.69
	St	37	1.33	0.75
1.d	MMA	13.3	1.18	0.81
	MA	9.4	1.21	0.88
	St	37	1.25	0.84
1.e	MMA	8.6	1.34	0.51
	MA	7.5	1.39	0.55
	St	27	1.44	0.67
1.f	MMA	11.6	1.31	0.52
	MA	7.7	1.38	0.58
	St	33	1.48	0.64

Table 2: Characteristics of the polymers formed with catalytic systems **1.c-f** (PDI = polydispersity index, f_i = Initiation efficiency = $M_{n,theor.}/M_{n,exp.}$ with $M_{n,theor.}$= $([monomer]_0/[initiator]_0)$ * MW(monomer) * conversion).

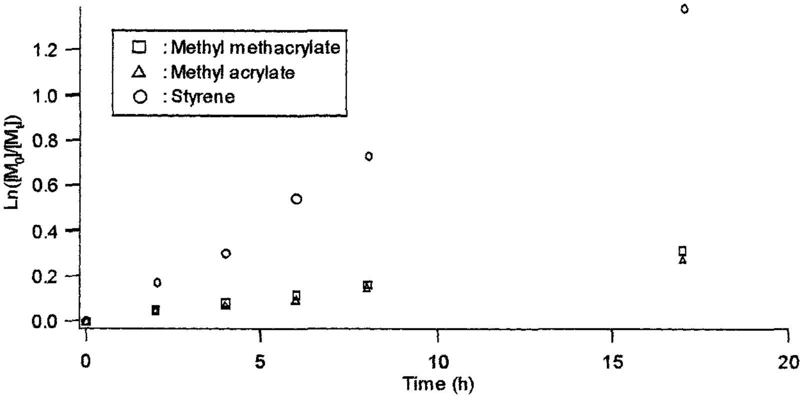


Figure 2: Time dependence of $\ln([M_0]/[M_t])$ for the ATRP of St, MA and MMA using catalytic system **1.d**. $[M_0]$ and $[M_t]$ are the monomer concentrations at times 0 and t. (Styrene: y = 0.0838 x; r^2 = 0.9931, Methyl acrylate: y = 0.0167 x; r^2 = 0.9831, Methyl methacrylate: y = 0.019 x; r^2 = 0.9931).

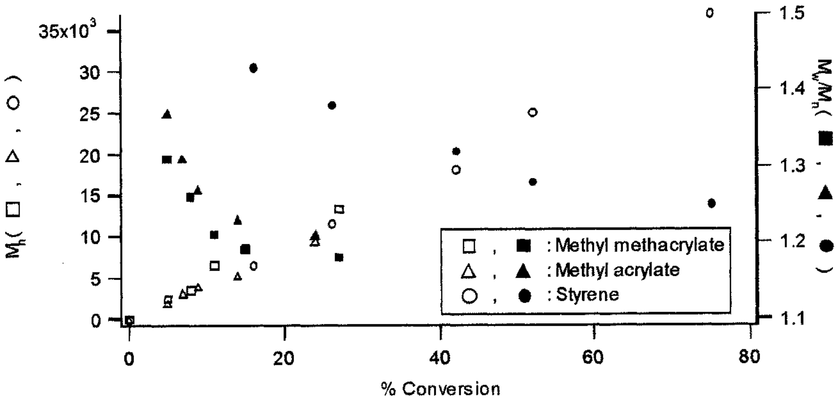


Figure 3: Dependence of the molecular weight M_n and M_w/M_n on monomer conversion for St, MA and MMA and using catalytic system **1.d**.

Secondly, we tested the ATRP activity of the cationic ruthenium alkylidene species **2.a-f** for some representative monomers. Complexes **2.a-f** were obtained by an in situ abstraction of chloride from systems **1.a-f** by addition of 1 equivalent silver tetrafluoroborate (figure 4). The polymerizations were performed both in toluene and a water/toluene mixture as solvent. Under vigorous stirring the polymerization with the latter solvent proceeded in a suspension system and this irrespective of the fact that we didn't add any suspension stabilizers (dispersants) to the reaction mixture. When the stirring was stopped, a regeneration of a two-layered mixture took place so that the polymers could be isolated from the upper organic phase.

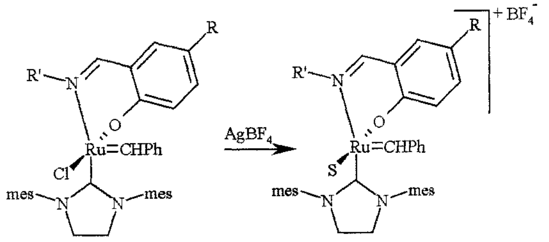


Figure 4: Depicture of the cationic ruthenium alkylidene complexes **2.a-f**.

The polymerization yields [%] with the cationic ruthenium alkylidene complexes **2.a-f** are summarized in table 3. The characteristics of the polymers obtained with these catalytic systems are depicted in table 4. When one compares the data gathered in tables 1 and 3, the first thing that catches the eye is the superior activity of the cationic complexes, irrespective of the solvent used. Furthermore, table 3 shows that for a certain catalytic system, the polymerization yields are systematically higher in the water/toluene mixture than in toluene. For example, the best system **2.d** converts MA, St and MMA in toluene in 33 %, 92 % and 84% yield, respectively, whereas in the water/toluene mixture the conversion increases to 42 %, 99 % and 97 %, respectively. Moreover, as can be seen by the higher PDI's of the formed polymers and the lower initiator efficiencies, the polymerization is also less controlled in toluene.

	Toluene						Toluene/Water					
	2.a	2.b	2.c	2.d	2.e	2.f	2.a	2.b	2.c	2.d	2.e	2.f
MMA	16	27	75	84	51	63	21	34	83	97	64	70
IBMA	12	20	63	77	33	45	18	25	80	90	42	57
MA	<5	7	22	33	10	18	9	13	35	42	9	23
BA	<5	<5	15	28	<5	5	<5	10	21	32	7	10
St	24	37	84	92	60	73	33	48	94	99	78	85

Table 3: Yield [%] for the ATRP of some representative vinyl monomers in a water/toluene mixture and toluene and catalysed by the cationic ruthenium alkylidene complexes **2.a-f** (MMA: methyl methacrylate, IBMA: isobutyl methacrylate, MA: methyl acrylate, BA: butyl acrylate, St: styrene).

		Toluene			Toluene/Water		
		M_n(x 10^3)	PDI	f_i	M_n(x 10^3)	PDI	f_i
2.a	MMA	13.6	1.75	0.47	15.3	1.52	0.55
	MA	--	--	--	--	--	--
	St	18.9	1.86	0.53	23	1.65	0.60
2.b	MMA	18.6	1.69	0.58	24	1.49	0.57
	MA	--	--	--	--	--	--
	St	25	1.83	0.61	30	1.54	0.66
2.c	MMA	56	1.63	0.54	54	1.39	0.62
	MA	13.1	1.68	0.58	18.5	1.43	0.65
	St	56	1.77	0.63	57	1.53	0.69
2.d	MMA	52	1.52	0.65	53	1.33	0.73
	MA	18.3	1.55	0.62	18.8	1.32	0.77
	St	58	1.60	0.66	54	1.36	0.76
2.e	MMA	42	1.71	0.49	55	1.47	0.47
	MA	7.8	1.76	0.44	--	--	--
	St	48	1.83	0.52	52	1.61	0.63
2.f	MMA	62	1.70	0.41	62	1.43	0.45
	MA	15.4	1.82	0.40	18	1.41	0.44
	St	62	1.88	0.49	62	1.57	0.57

Table 4: Characteristics of the polymers formed with the catalytic systems **2.a-f** using a water/toluene mixture and toluene as solvent.

To elaborate if in this case all the criteria of a controlled radical polymerization are fulfilled, the time course of the polymerization with the best system **2.d** was followed for three different monomers using the water/toluene mixture as solvent. The plots of $\ln([M_0]/[M_t])$ versus time (figure 5) and M_n versus monomer conversion (figure 6) are linear for all three monomers. Together with the decrease of the PDI's of the polymers with monomer conversion (figure 6), the above-mentioned features confirm the "living" character of the radical polymerization.

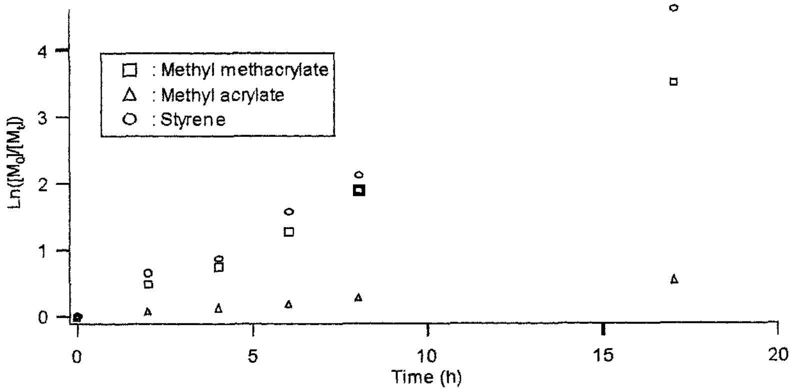


Figure 5: Time dependence of ln($[M_0]/[M]_t$) for the ATRP of St, MA and MMA using catalytic system **2.d** and using a water/toluene mixture as solvent. $[M_0]$ and $[M_t]$ are the monomer concentrations at times 0 and t. (Styrene: y = 0.2675 x; r^2 = 0.9954, Methyl acrylate: y = 0.0329 x; r^2 = 0.9936, Methyl methacrylate: y = 0.2113 x; r^2 = 0.9919).

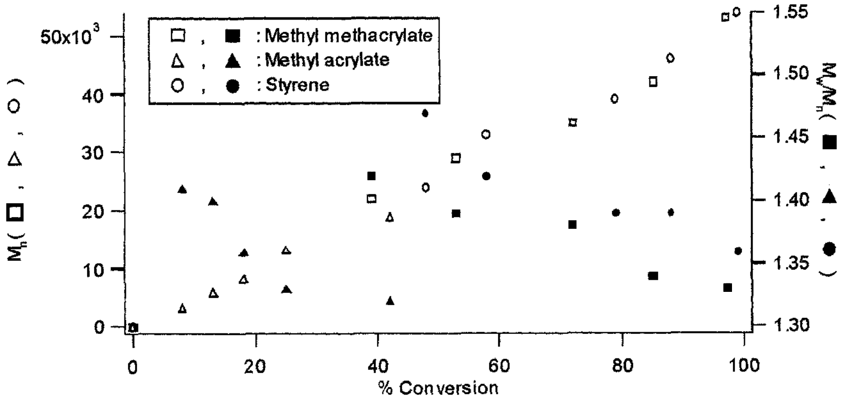
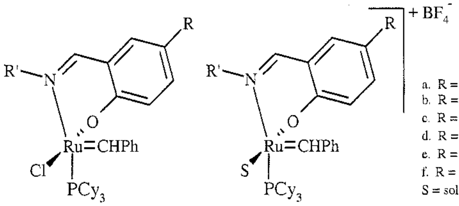


Figure 6: Dependence of the molecular weight M_n and M_w/M_n on monomer conversion for St, MA and MMA and using catalytic system **2.d** and using a water/toluene mixture as solvent.

Recently, we published an article dealing with the ATRP activity of analogues neutral and cationic complexes bearing a Schiff base and a tricyclohexyl phosphine ligand (figure 7, **3.a-f** and **4.a-f**) [5]. Comparing the results of these systems with the results of complexes **1.a-f** and **2.a-f**, leads to the exposure of the following interesting features: i) in both cases the activity of the cationic systems was much higher than for the neutral complexes, ii) the adventitious effect on the control over the radical polymerization process when using the cationic complexes with a water/toluene mixture as solvent, was observed very clearly in both cases, iii) the influence of using the water/toluene mixture as solvent on the activity of the cationic complexes is opposite for both types of catalysts: whereas for the cationic systems **4.a-f** the activity decreases in the biphasic reaction environment, systems **2.a-f** show a markedly increase of activity when water/toluene mixtures are used as polymerization solvent, iv) for both type of catalysts the **d-configuration** of the Schiff base ligand gives rise to formation of the most performing catalytic systems and this irrespective of the fact whether the systems are neutral or cationic and v) whereas MMA and St are polymerized in higher yields and in a more controlled way by the ruthenium Schiff base complexes bearing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligand, MA shows an opposite behavior; here the complexes bearing the tricyclohexyl phosphine ligand exhibit the highest activity and control over the radical polymerization process. This last point is a confirmation of the fact that in atom transfer radical polymerization, each monomer has its own specific needs concerning the steric and electronic optimization of the catalyst structure [1g-j].



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a. R = H, R' = Me
b. R = NO_2, R' = Me
c. R = H, R' = 2,6-Me-4-BrC_6H_2
d. R = NO_2, R' = 2,6-Me-4-BrC_6H_2
e. R = H, R' = 2,6-$iPrC_6H_3$
f. R = NO_2, R' = 2,6-$iPrC_6H_3$
S = solvent

Figure 7: Structure of analogues neutral and cationic Schiff base containing ruthenium complexes for which we already reported their activity in controlled radical polymerizations.

Conclusions

In conclusion, we have demonstrated that the Schiff base and 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene containing ruthenium alkylidene catalysts **1.a-f** exhibit moderate activities in ATRP reactions. However, if a chloride is abstracted from the neutral complexes, a spectacular improvement of the activity is observed. The resulting cationic Ru-alkylidene complexes **2.a-f** are also capable of performing controlled radical polymerisations in water/toluene mixtures with good control.

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