



RuCl₂(PPh₃)₂(triazol-5-ylidene): an active catalyst for controlled radical polymerization of methyl methacrylate in the presence of primary or secondary amines

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Abstract

RuCl₂(PPh₃)₂(triazol-5-ylidene) (**4**) induces, in the presence of primary or secondary amines and in conjunction of an organic bromide initiator (ethyl-2-bromo-isobutyrate), a controlled radical polymerization of methyl methacrylate (MMA). The optimal concentration of both the primary amine (CH₃CH₂CH₂NH₂) and the secondary amine (*n*Bu₂NH) is determined as a catalyst/amine ratio of 1/4. Polymers obtained, in the presence of both amines, have very narrow molecular weight distributions (MWD), 1.08 and 1.43 for the primary and secondary amine, respectively. The best initiation efficiency was obtained for the **4**/initiator/*n*Bu₂NH (1/1/4) initiating system (93%). This system yields polymers with a very narrow MWD (1.24) and with a controlled *M_n* in direct proportion to the monomer conversion within a 24 h time period. NMR analysis reveals that the added amines interact with the Ru-complex **4** to generate a highly active catalyst for the polymerization of MMA. The controlled character of the polymerization is established via a monomer-addition experiment and ¹H NMR analysis. The microstructure of the synthesized polymers (syndiotactic) is in agreement with that of the free radical polymerization. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Atom transfer radical polymerization (ATRP); Ruthenium complex; Methyl methacrylate; Amine additives; Triazol-5-ylidene

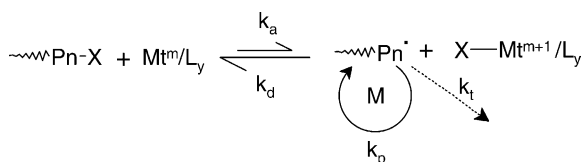
1. Introduction

Nearly 50% of industrial polymers are synthesized according to the radical polymerization method [1]. The commercial success is based on the possibility of polymerizing a broad variety of monomers at mild reaction conditions. Despite the high potential of the free radical polymerization, a lack of control limits their application in precise polymer synthesis.

Unlike the ionic counterpart, side reactions such as disproportionation and coupling determine the polymerization process. The demand for a controlled radical polymerization, which combines the advantages of the free radical polymerization and the controlled ionic polymerization, gave rise to the development of the so-called controlled free radical polymerization (CFRP) methods. The three most important methods are known as nitroxide mediated polymerization [2], atom transfer radical polymerization (ATRP) [3–5] and reversible addition fragmentation chain transfer (RAFT) [6]. All methods are based on the fast interconversion between the radical species and the dormant species, with the equilibrium shifted towards the

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Scheme 1.

dormant species whereby bimolecular side reactions are suppressed. The faster interaction of the radical species compared to the rate of propagation guarantee a narrow molecular weight distribution of the synthesized polymers. For the transition metal catalyzed polymerization, i.e. ATRP, the dormant species during the polymerization involves a carbon–halogen bond (R–X). The controlled polymerization proceeds via the reversible metal mediated activation–deactivation of the dormant C–X bonds at the polymer chain end originating from the halide as initiator (Scheme 1).

Most of the transition metals complexes, which exhibit reactivity, are metal halides of Ru(II) [7–12], Cu(I) [13–16], Fe(II) [17–20], Ni(II) [21–24], Rh(I) [25–27], Pd(II) [28] and Re(V) [29], and zero valent metals such as Pd(0) and Ni(0) [30]. A major advantage is the possibility to tune the transition metal complexes by the design of the ligand structure (Scheme 2).

A way to improve the catalytic activity is to increase the electron density on the metal center by substitution with more electron donating ligands. Substitution of a triphenylphosphine by the more electron donating indenyl ligand provides a more active catalyst than its dichloride counterpart $\text{RuCl}_2(\text{PPh}_3)_3$ (**1** and **2**) [31]. Addition of $\text{Al}(\text{O}-i\text{Pr})_3$ or amines ensures an additional increase in rate, with preservation of the narrow polydispersity [32]. Since 1992, *N*-heterocyclic carbenes (NHC) have emerged as

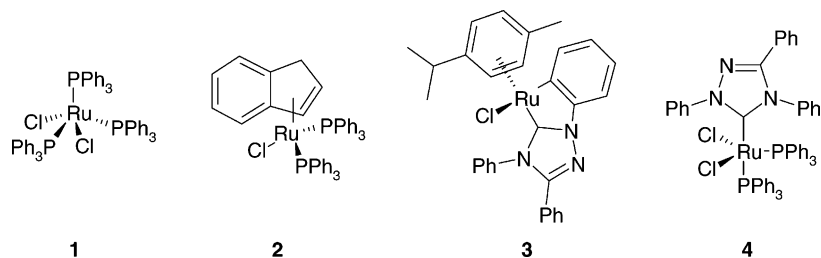
excellent substitutes for the less stable phosphine ligands. For the ATRP reaction, improved catalytic activity is shown for the Fe–(FeX₂(imidazolylidene)₂) and Ru–(RuCl(*p*-cymene)triazol-5-ylidene) (**3**) complexes [33–35].

In this paper, we report that the triazol-5-ylidene derivative (**4**) of **1** shows a marked reactivity and activity for the controlled radical polymerization in the presence of amine additives [36]. The catalyst/*n*Bu₂NH induces a smooth controlled radical polymerization of MMA in conjunction with organic halides to produce polymers of narrow molecular weight ($M_w/M_n \sim 1.2$).

2. Experimental

2.1. General remarks

All reactions were performed under inert atmosphere using Schlenck techniques. NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. The molecular weights and the molecular weight distribution of the polymers were determined by gel permeation chromatography (CHCl₃, 35 °C) using a Shimadzu CLASS-VP™ system equipped with three serial placed columns (PSS SDV: 30 cm, Ø = 8 mm, 10³, 10⁴, 10⁵ Å) and the calibration using poly-MMA standards. Toluene, pentane and toluene-d₈ (obtained from Acros) are dried over Na, CDCl₃ (obtained from Acros, 96.9 at.% D) is dried over molecular sieves (MS4A). $\text{RuCl}_2(\text{PPh}_3)_3$, 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene, CH₃CH₂CH₂NH₂, *n*Bu₂NH, Et₃N, ethyl-2-bromoisobutyrate (obtained from Acros) were used without further purification. Methyl methacrylate (MMA) (obtained from Acros) was freshly distilled prior to use.



Scheme 2.

2.2. General polymerization procedure

In a typical ATRP experiment 0.0117 mmol of catalyst was placed in a glass tube (in which air was expelled by three vacuum-nitrogen cycles) containing a magnet stirring barr and capped by a three-way stopcock and dissolved in toluene. Then the monomer (MMA) and initiator (ethyl-2-bromo-isobutyrate) were added so that the molar ratios [catalyst]/[initiator]/[monomer] were 1/1/806. All liquids were handled under argon with dried syringes. The reaction mixture was heated for different time periods at 85 °C. After cooling to room temperature, the reaction is diluted in THF and poured into 50 ml *n*-heptane under vigorous stirring. The precipitated polymer is filtered and dried in vacuum overnight.

2.3. Polymerization procedure with amine additives

Catalyst (0.0117 mmol) was placed in a glass tube (in which air was expelled by three vacuum-nitrogen cycles) containing a magnet stirring barr and capped by a three-way stopcock and dissolved in toluene. Then the monomer (MMA), initiator (ethyl-2-bromo-isobutyrate) and respective amine (CH₃CH₂CH₂NH₂; *n*Bu₂NH; Et₃N) were added so that the molar ratios [catalyst]/[initiator]/[monomer]/[amine] were 1/1/806/*x*. The same procedure as described in the general procedure is followed.

2.4. Monomer-addition experiment

The same preparation as described in Section 2.3 is conducted. The reaction is stirred at 85 °C until all added monomer is consumed. A second and equal amount of MMA is added under argon. The reaction is stopped at different time periods. The same procedure to isolate the polymers as described in the general procedure is followed.

2.5. NMR analysis of interaction between complex 4 and amines

In a glove box, a 5 mm Wilmad NMR tube is charged with complex **4** (0.02 mmol), the respective amine (0.08 mmol) and CDCl₃ (1 ml). The reaction is followed by ³¹P-{¹H}-NMR analysis, which are referred to a H₃PO₄ standard.

3. Results and discussion

3.1. Controlled polymerization of MMA

MMA was polymerized with the triazol-5-ylidene derivative **4** in conjunction with ethyl-2-bromo-isobutyrate as an initiator and the absence of amine additives in toluene at 85 °C. The reaction only yields 3.3% conversion after 5 h of reaction. A series of amine additives were added to the reaction mixture and lead to a smooth polymerization of MMA. Primary and secondary amines accelerate the polymerization reaction dramatically, whilst the tertiary amine completely blocks the reaction. A similar rate enhancement has been reported for the Ru-complexes **1** and **2** [32,37]. To determine the optimal amine species and concentration, different amounts of the three types of amines are added (Table 1).

Addition of the primary amine, CH₃CH₂CH₂NH₂, produces polymers with a very narrow MWD (M_w/M_n) (1.08 < MWD < 1.44). The conversion and MWD are somewhat decreased when *n*Bu₂NH is added, but higher initiator efficiency factors for the catalyst **4** are obtained. Addition of a tertiary amine blocks the polymerization completely. Comparing the initiation efficiency of the catalyst **4**, the best result is obtained when **4** equivalents of a secondary amine are added. Here, 93.9% of the added Ru-complex acts as an actual catalyst for the controlled polymerization of MMA.

The polymerization of MMA is performed in the presence of **4** equivalents of *n*Bu₂NH in toluene at 85 °C (Fig. 1). The M_n of the polymers obtained increases in direct proportion to the monomer conversion. The obtained data are close to the calculated values, which assume that each initiator molecule produces one polymer chain. The linear correlation between $\ln([M]_0/[M])$ and time ($r^2 = 0.98$) clearly indicates that the concentration of radicals remains constant during the polymerization of MMA and that the ATRP of MMA in the presence of **4**/*n*Bu₂NH proceeds in a controlled manner. Thus, the addition of **4** equivalent of *n*Bu₂NH delivers a rate enhancement and controlled molecular weights for the radical polymerization.

To investigate the living character of the MMA polymerization with the secondary amine *n*Bu₂NH, a second feed of monomer is added to the reaction mixture at the point where nearly all initial monomer of the first batch is consumed (Fig. 2).

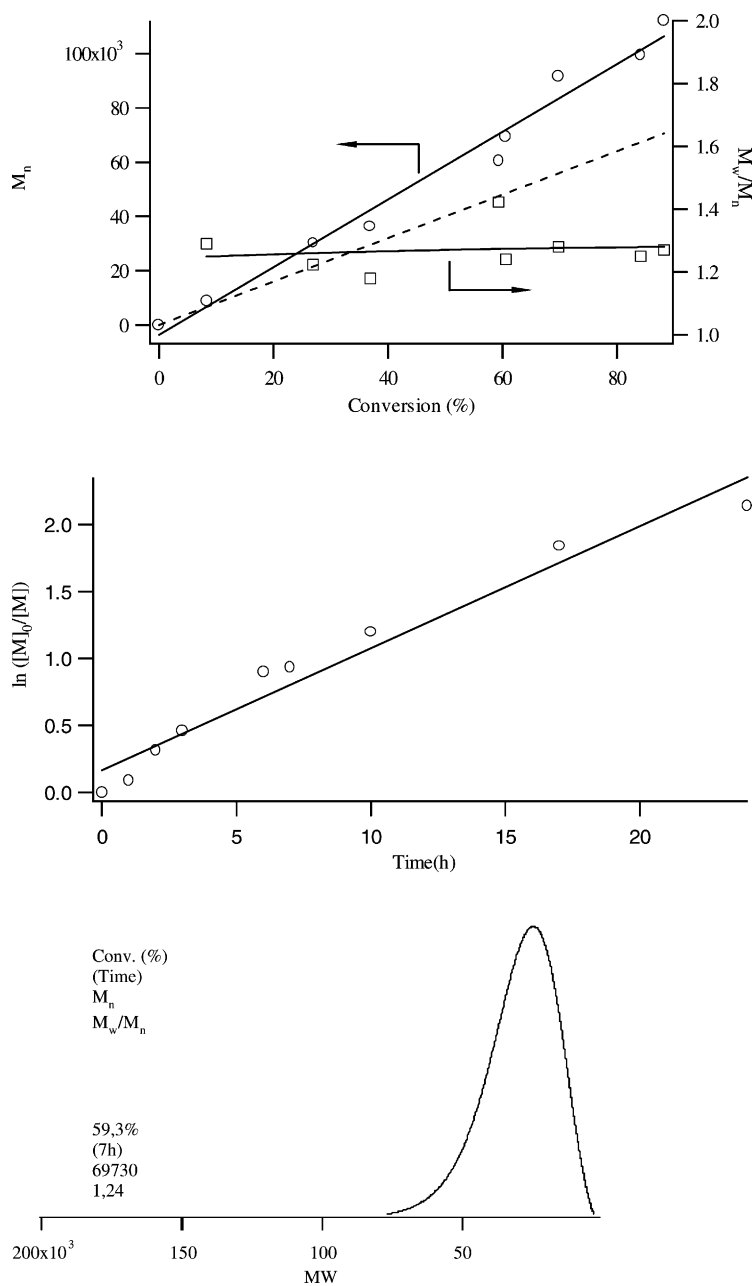


Fig. 1. M_n , M_w , M_w/M_n and GPC curves and $\ln([M]_0/[M])$ vs. time plot ($r^2 = 0.98$) of PMMA obtained with $4/n\text{Bu}_2\text{NH}$ in toluene at 85°C : $[\text{MMA}]_0/[\text{I}]/[\text{catalyst}]/[n\text{Bu}_2\text{NH}] = 806/1/1/4$.

The added monomer is polymerized smoothly. After 48 h, 62.9% of the second monomer feed is converted. The obtained polymers show an unimodal and narrow MWD (1.24). The values of the M_n decrease propor-

tional to the converted monomer, even after an addition of a fresh batch of monomer. The polymerization does not lose its controlled character, since the $\ln([M]_0/[M])$ versus time plot ($r^2 = 0.98$) remains linear.

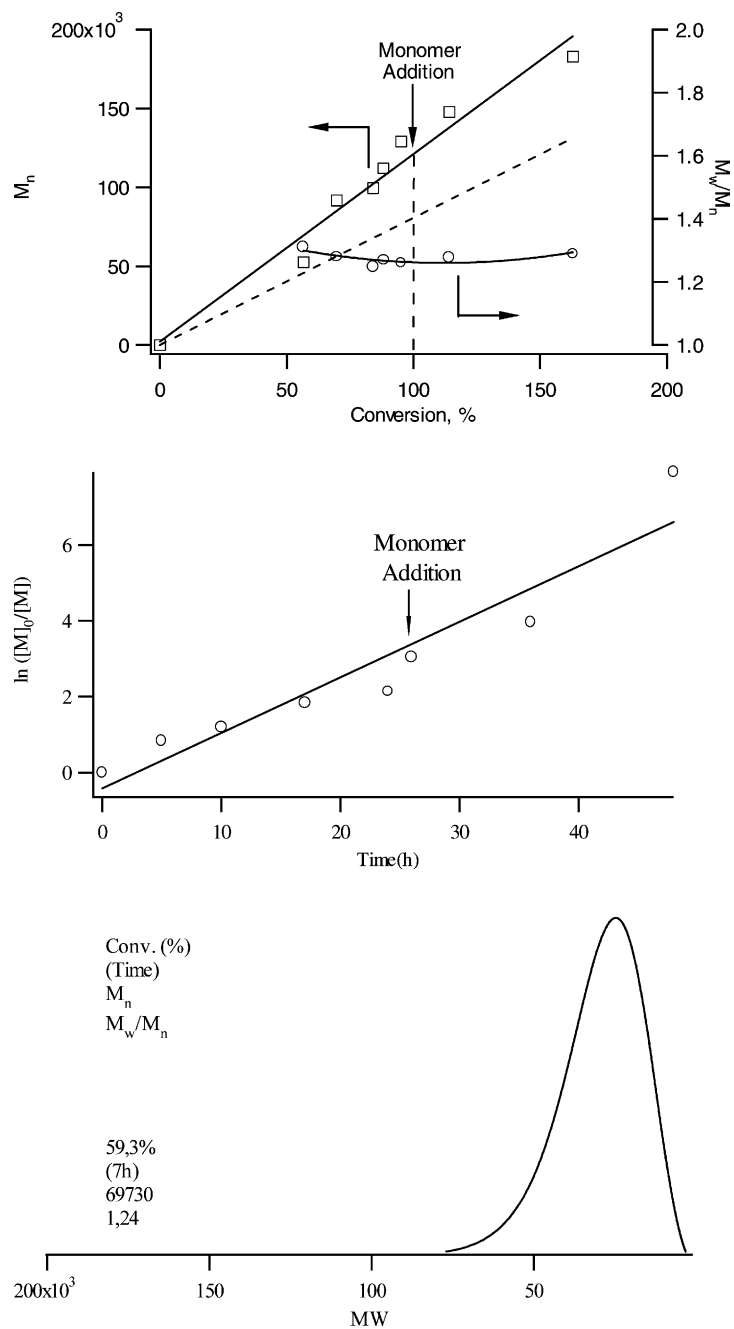


Fig. 2. M_n , M_w , M_w/M_n and GPC curves and $\ln([M]_0/[M])$ vs. time plot ($r^2 = 0.98$) of PMMA obtained for a monomer-addition experiment with $4/n\text{Bu}_2\text{NH}$ in toluene at 85°C : $[\text{MMA}]_0 = [\text{MMA}]_{\text{add}}/[\text{I}]/[\text{catalyst}]/[n\text{Bu}_2\text{NH}] = 806/1/1/4$.

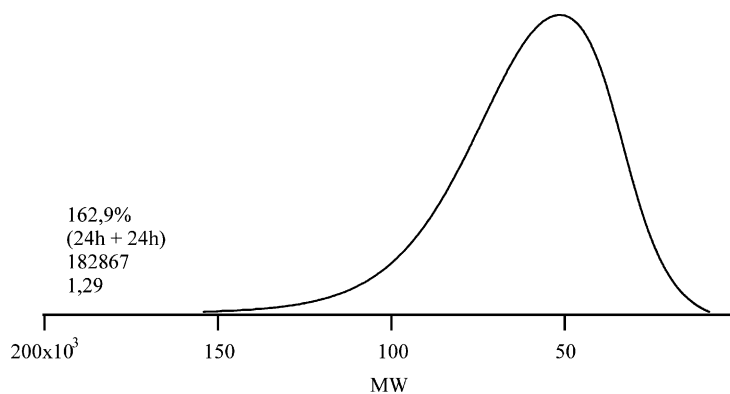


Fig. 2. (Continued).

3.2. NMR analysis of interaction between complex **4** and amines

Via $^{31}\text{P}\{-\text{H}\}$ -NMR analysis the interaction between complex **4** and the two rate enhancing amines, i.e. propylamine and *n*-dibutylamine, is investigated. To

a solution of **4** in CDCl_3 are added 4 equivalents of the respective amine. The $^{31}\text{P}\{-\text{H}\}$ -NMR spectra are shown in Fig. 3.

For the catalyst **4**, a signal at 30.2 ppm is detected and no evidence for free phosphine ligands is found (Fig. 3a). Unlike the parent $\text{RuCl}_2(\text{PPh}_3)_3$ (**1**)

Table 1

Influence of amines on the polymerization of MMA in toluene at 85 °C after 5 h; $[\text{MMA}]:[\text{I}]^{\text{a}}:[\text{RuCl}_2(\text{PPh}_3)_2(\text{triazol-5-ylidene})]:[\text{amine}] = 806:1:1:x$

Amine	[Catalyst]:[amine]	Yield (%) ^b	M_n^c	M_w^c	M_w/M_n	$M_{n,\text{theor}}^d$	f^e
Primary amine	1:0	3.3	f	f			
	1:2	27.4	28330	30668	1.08	22111	78.0
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	1:4	56.7	52496	68789	1.31	45755	87.2
	1:6	67.6	82678	111958	1.35	54551	66.0
	1:8	65.4	104375	117015	1.12	52776	50.6
	1:10	59.8	132705	185804	1.40	48257	36.4
Secondary amine	1:0	3.3	f	f			
	1:2	34.9	33737	49281	1.46	28163	83.5
<i>n</i> Bu ₂ NH	1:4	45.2	38844	57637	1.48	36475	93.9
	1:6	47.7	52978	76602	1.45	38492	72.7
	1:8	52.7	56782	81245	1.43	42527	74.9
	1:10	59.8	60504	94158	1.56	48257	79.8
Tertiary amine	1:0	3.3	f	f			
	1:2	0.5	f	f			
Et ₃ N	1:4	0.9	f	f			
	1:6	0.5	f	f			
	1:8	0.8	f	f			
	1:10	0.9	f	f			

^a Ethyl-2-bromo-isobutyrate.

^b Yield as determined by gravimetric analysis.

^c M_n and M_w as determined with GPC analysis calibrated with PMMA standards.

^d $([\text{MMA}]_0/[\text{initiator}]_0) \times \text{conversion}_t \times \text{MW}_{\text{MMA}}$.

^e Efficiency factor (%) = $(M_{n,\text{theor}}/M_n) \times 100$.

^f Yield is too low to determine the appropriate molecular weights.

complex, which acts as a dinuclear complex in solution and release of phosphines is detected in the solution [37]. This leads to the conclusion that complex **4** does not form a dinuclear complex but exists as a mononuclear product in solution. In contrary to results for the indenyl-Ru-complex described by Sawamoto et al., this does not result in a very high activity [31]. Complex **4** does not show any activity in the absence of amines. With the addition of 4

equivalent of primary amine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, one additional peak appears at -4.3 ppm attributed to free phosphine (Fig. 3b). No significant change occurs for the signal of the Ru-complex. In contrast, the added $n\text{Bu}_2\text{NH}$ leads to the formation of a new phosphorus containing species (33.9 ppm) and no release of a phosphine ligand is detected. Therefore, the secondary amine co-ordinates to the Ru-complex to form a new complex that possesses a very high activity. Similar,

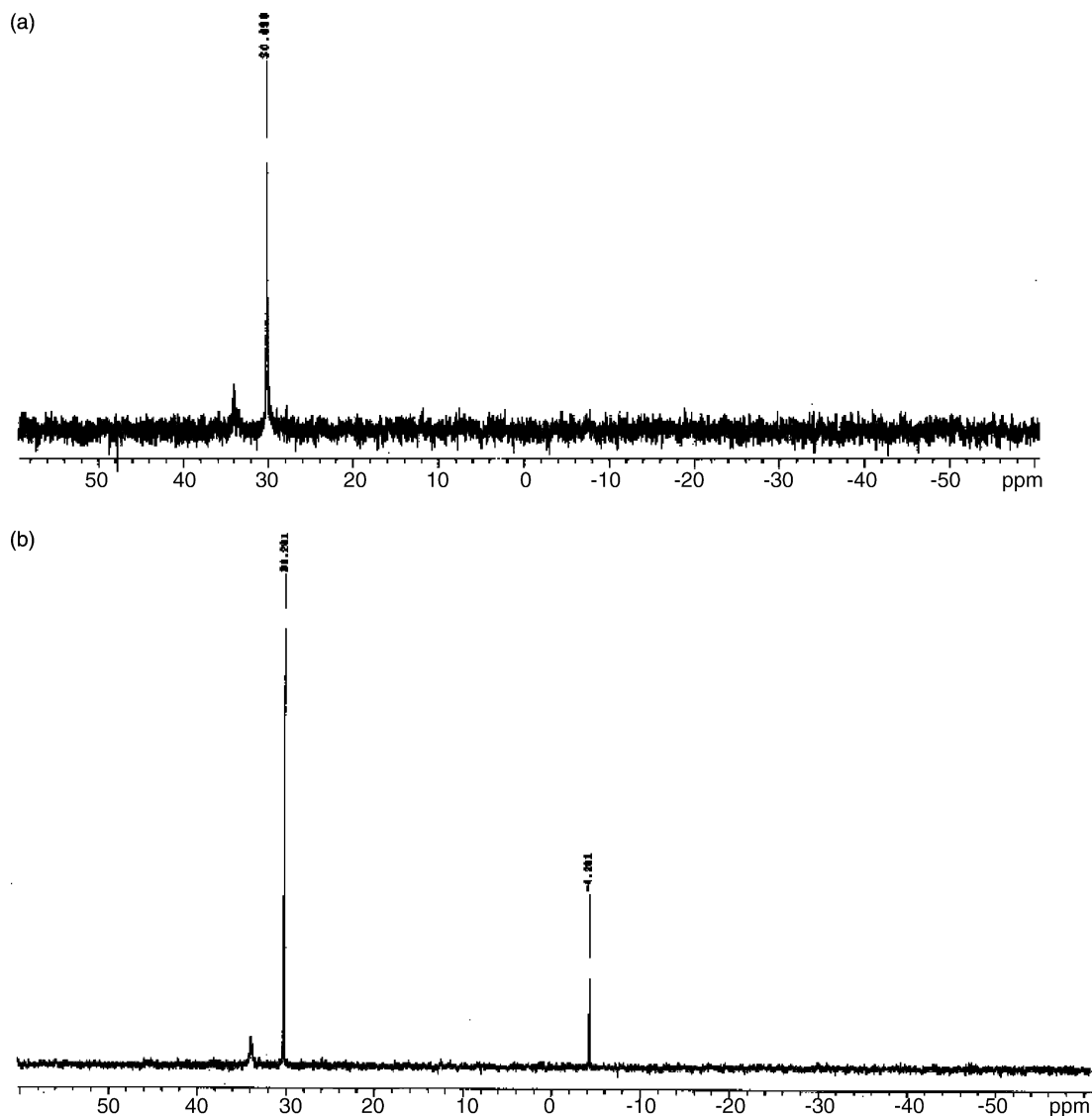


Fig. 3. $^{31}\text{P}\{-\text{H}\}$ -NMR analysis of (a) Ru-complex **4** in CDCl_3 at 25°C ; (b) Ru-complex **4** and 4 equivalents of $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ in CDCl_3 at 25°C ; (c) Ru-complex **4** and 4 equivalents of $n\text{Bu}_2\text{NH}$ in CDCl_3 at 25°C .

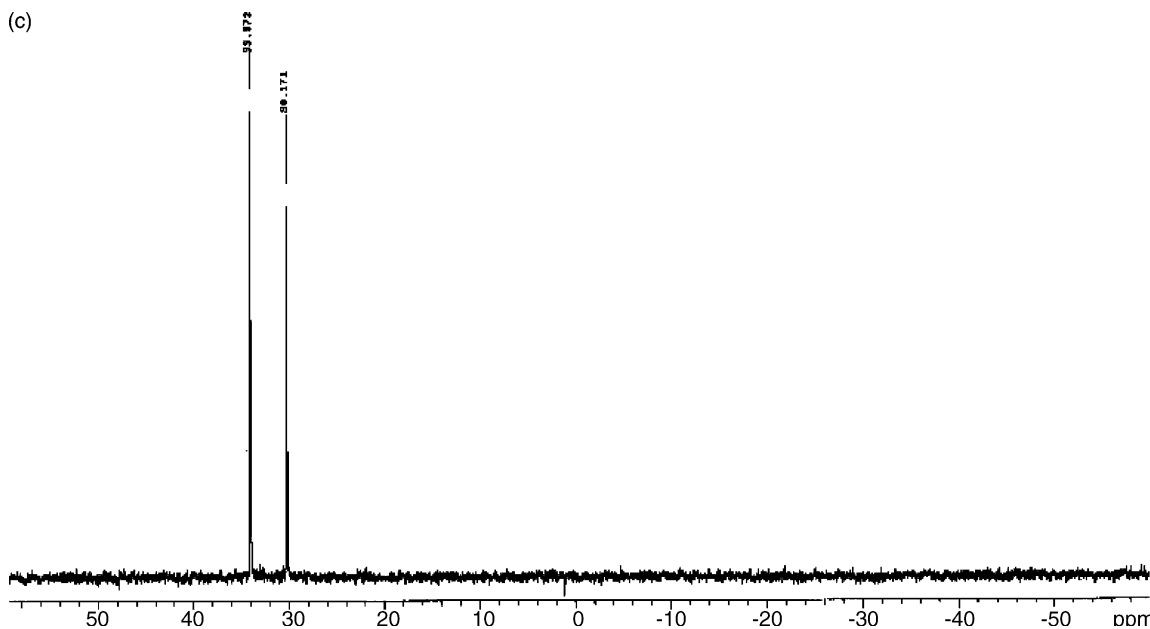


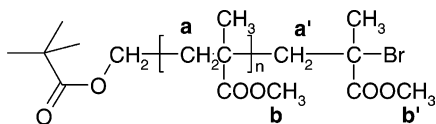
Fig. 3. (Continued).

addition of the primary amine gives rise to a dramatic rate enhancement. Here, only the release of a phosphine ligand can attribute to the increased activity. Both amine additives interact with the Ru-complex **4** and generate a highly active catalytic system for the controlled polymerization of MMA.

3.3. Microstructure and endgroup functionality of the synthesized polymer

The polymerization of MMA catalyzed by **4**/*n*Bu₂NH/ethyl-2-bromo-isobutyrate is followed in situ by ¹H NMR at 85 °C in toluene-d₈.

Next to the large absorption of the signals of the poly-MMA chain units (**a** and **b**), small signals of the initiator appear (**a'** and **b'**) attributed to the methylene and acetate endgroup adjacent to the bromine atom at the ω-end (Scheme 3) [38]. Due to overlap of sig-



Scheme 3.

nals of the *t*-butyl group and signals of the poly-MMA chain, no abstraction of the end functionality at the α-end is possible. The number average degree of the polymerization (DP_n) obtained from the peak integration, $(b + b'/a') = 167$, assuming that each initiator molecule induces one polymer chain. This is in agreement with the $(DP_n(\text{GPC}) = 185)$ calibrated with standard poly-MMA samples. The number average end functionality at the ω-end, which is given by the ratio $DP_n(\text{GPC})/DP_n(\text{NMR})$ is 1.11. This means that the polymerization proceeds via activation of the C–Br bond originated from the ethyl-2-bromo-isobutyrate initiator by the Ru-complex **4** and does not proceed via insertion in a possible Ru–C bond. Between 5 and 6 ppm, small signals characteristic to an olefinic endgroup originating from disproportionation between the polymer chains. The olefin content only reaches a merely 1%, so most of the polymer endgroups consist of a Br atom. ¹³C NMR analysis reveal that a mainly syndiotactic polymer is obtained.

4. Conclusion

Addition of primary and secondary amine to the RuCl₂(PPh₃)₂(triazol-5-ylidene)/ethyl-2-bromo-

isobutyrate initiating system provides a highly active catalyst for the controlled radical polymerization of methyl methacrylate. Polymers with a very narrow molecular weight distribution ($MWD = 1.24$) are obtained within 24 h of reaction.

Acknowledgements

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