Neutral Pd(II) and Ni(II) acetylide catalysts for the polymerization of methyl methacrylate

Hongmei Sun [a,*], Qi Shen [a], Xingan Peng [a], and Mujie Yang [b]

[a] *Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, China*
[b] *Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China*

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Homogenous polymerization of methyl methacrylate using Pd(II)- and Ni(II)-based acetylide complexes as initiators has been investigated. $M(PR'_3)_2(C{\equiv}CR)_2$ (M = Pd, Ni; R′ = PPh_3, P*n*-Bu_3; R = Ph, CH_2OH, CH_2OOCCH_3, CH_2OOCPh, $CH_2OOCPhOH$-*o*) were found to be a novel type of effective initiators for the polymerization of methyl methacrylate. Among them, $Pd(C{\equiv}CPh)_2(PPh_3)_2$ (PPP) shows the highest activity in the MMA polymerization and the PMMA obtained is a syndiotactic polymer with high number-average molecular weight (M_n) of 14.1×10^4. Some features and kinetic behavior of MMA polymerization initiated by PPP were studied in detail. The polymerization reaction is first-order with respect to both [PPP] and [MMA]. Radical polymerization mechanism is proposed.

KEY WORDS: polymerization; methyl methacrylate; late transition metal acetylide; catalyst.

1. Introduction

Recently, a great deal of attention has been directed towards the research of late transition metal-based complexes used as polymerization catalysts, in particular, both as insertion-type olefin polymerization catalysts [1] and as atom transfer radical polymerization (ATRP) catalysts [2]. Relative to early metals, late metals are typically less oxophilic and thus more functional-group tolerant. For example, Brookhart's cationic Pd(II) α-diimine complexes have been developed to catalyze the copolymerization of ethylene and α-olefins with commercially significant, functionalized olefins such as methyl acrylate to give high molecular weight, random copolymers in CH_2Cl_2 under mild conditions [3]. In addition, similar nickel α-diimine complexes showed somewhat lower functional-group tolerance than palladium ones and catalyzed ethylene polymerization in the presence of low levels of methyl acrylate, and gave a copolymer showing an acrylate content of 0.1 mol% [1]. This development might potentially offer a new low-pressure, low-temperature route to a wide range of commercially available copolymers. In these reactions, acrylate insertion occurred predominantly in a 2,1-fashion and the strong binding of oxygen to the metal center retarded the rate of chain growth, so most of the ester groups were located at the ends of branches.

Alternatively, Ni(II)-based catalysts, *i.e.* $NiBr_2(PPh_3)_2$ [4] and $NiBr_2(Pn\text{-}Bu_3)_2$ [2h], were found to induce new living radical polymerization (also called ATRP) of methyl methacrylate (MMA) in the presence of organic halides as an initiator (such as CCl_4 or CCl_3Br) and $Al(Oi\text{-}Pr)_3$ as additive. These systems gave polymers with controlled molecular weights and narrow molecular weight distributions. In these reactions, a carbon radical is generated from the C–X bond of an organic halide via a series of consecutive reversible redox reactions between Ni(II) and Ni(III) species (scheme 1). However, these polymerizations are very sensitive to water and occurred at $\geq$80 °C. Recently, Lecomte *et al.* [2i] reported the first example of an active catalyst prepared from palladium acetate, $Pd(OAc)_2$, PPh_3, and CCl_4, for controlled radical polymerization of MMA at 70 °C, not only in organic solvents but also in the presence of water. The role of PPh_3 is to saturate the metal coordination sites, avoiding formation of black slurry of metallic palladium during the reaction process. However, a large amount of $Pd(OAc)_2$ was used in a 10-fold molar excess with respect to CCl_4. In fact, although an increasing number of transition metals (*e.g.* Cu, Ru, Fe, Ni) [2] in conjunction with different ligands can be used to catalyze this type of polymerization, a steady effort is directed toward developing new metals and new ligands with improved activities, to perform the polymerization with fewer metal complexes or at a range of lower temperature from 40 to 80 °C.

In general, transition metal to alkyl or aryl M–C σ-bond is unstable at room temperature as well as being air- and water-sensitive. However, if both strongly π-bonding ligands such as phosphine and the carbon σ-bonded to the transition metal involved in an acetylenic bond are present in the molecule, then stable alkynyls can be prepared, *e.g. trans*-$(PPh_3)_2Pd(C{\equiv}CPh)_2$ [5]. In recent years, some transition metal acetylides were

* To whom correspondence should be addressed.
E-mail: sunhm68@sina.com

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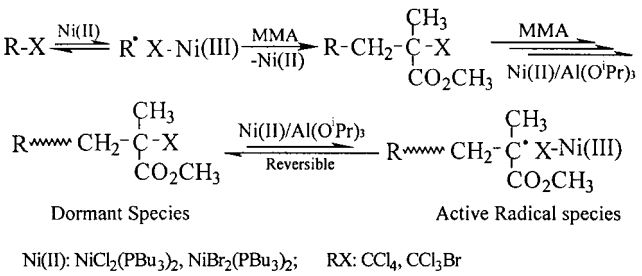

Scheme 1

found to be active catalysts for alkyne cyclotrimerization or polymerization [6]. In these reactions, a coordination/insertion mechanism has been suggested. The polymer chain was assumed to begin by insertion of a metal center π-coordinated monomer in the metal–alkynyl bond. We also reported the development of highly active Pd(II) and Ni(II) acetylide complexes $(PR'_3)_2M(C{\equiv}CR)_2$ [M = Pd, Ni; R′ = PPh_3, P*n*-Bu_3; R = Ph, CH_2OH, CH_2OOCCH_3, CH_2OOCPh, $CH_2OOCPhOH$-*o*, $C{\equiv}CC_6H_4C{\equiv}CH$] that polymerized polar alkynes, *e.g.*, propargyl alcohol (OHP) [7]. A key feature of these Pd or Ni complexes is their unique stability and then great functional-group tolerance. For example, the OHP polymerization is not sensitive either to the presence of water in solvent or oxygen in polymerization atmosphere. But up to now, these titled complexes have not been tried for the polymerization of polar vinyl monomer, especially MMA. Thus we describe here the first full account of the characteristic and mechanistic aspects of the homogeneous polymerization of MMA using a series of neutral Pd(II) and Ni(II) acetylide complexes as initiators.

2. Experimental

2.1. Materials

All solvents were analytical grade and dried with activated alumina. MMA was dried over CaH_2 and distilled under N_2 atmosphere at reduced pressure. Diethylamine was dried over CaH_2 and distilled under N_2 atmosphere. Triphenylphosphine (PPh_3) and azobis(isobutyronitrile) (AIBN) were recrystallized from 95% ethanol. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) (Aldrich) and tri-*n*-butylphosphine (P*n*-Bu_3) (Tokyo Kasei) were used as received. Eleven transition metal acetylides:

$Pd(PPh_3)_2(C{\equiv}CH)_2$ (PPE) [5],
$Pd(PPh_3)_2(C{\equiv}CPh)_2$ (PPP) [5],
$Pd(PPh_3)_2(C{\equiv}CCH_2OH)_2$ (PPO) [9],
$Pd(PPh_3)_2(C{\equiv}CCH_2OOCCH_3)_2$ (PPA) [10],
$Pd(PPh_3)_2(C{\equiv}CCH_2OOCPh)_2$ (PPB) [8],
$Pd(PPh_3)_2(C{\equiv}CCH_2OOCPhOH\text{-}o)_2$ (PPS) [8],
$Ni(PPh_3)_2(C{\equiv}CPh)_2$ (NPP) [11a],
$Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$ (NPD) [11b],
$Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)Cl$ (NPDCl) [11b],
$Pd(Pn\text{-}Bu_3)_2(C{\equiv}CPh)_2$ (PBP) [8], and
$Ni(Pn\text{-}Bu_3)_2(C{\equiv}CPh)_2$ (NBP) [12]
were prepared according to the literature.

2.2. Polymerization of MMA

As a general procedure, under dry nitrogen, the solvent $CHCl_3$ and MMA were added into a dry glass ampoule containing the solid initiator in turn. Then, the sealed ampoule was placed in a water bath held at the desired temperature. After a specific time, the polymerization was stopped by adding 1 ml of 2% HCl/ethanol. The resultant polymer was dissolved in THF, followed by precipitation in 95% ethanol. After filtration, the white polymer was dried in vacuum at 30 °C for 24 h. The conversion of polymerization was determined gravimetrically.

2.3. Oligomers for end-group characterization

The oligomerization of MMA was carried out with $Ni(Pn\text{-}Bu_3)_2(C{\equiv}CPh)_2$ (NBP) in CCl_3Br at 60 °C when [MMA] and [MMA]/[NBP] are 3.13 mol/l and 30, respectively. The reaction was terminated by adding 1 ml of 10% HCl/EtOH after 4 h of oligomerization. The quenched reaction solution was evaporated to dryness to give a solid product, which was subsequently diluted with toluene (~5 ml). The diluted solution was washed with water and evaporated to dryness to give the products, which were subsequently dried overnight under vacuum at room temperature.

2.4. Characterizations

The elemental analyses were carried out by a Carloerba Model 1106 elemental analyzer. Melting points were determined on a Yanaco MP-500 melting point apparatus. The molecular weights of PMMA (M_n and M_w) and the polydispersity index (M_w/M_n) were measured on a Waters 208 gel permeation chromatograph with three μ-styragel linear columns (10^5, 10^4, and 10^3 Å) *versus* polystyrene standard, in THF at 25 °C. ^{1}H-NMR spectra were taken on a Brucker Avance DMX500 (500 MHz) spectrometer in $CDCl_3$ at 25 °C, using tetramethylsilane as the internal reference. ^{1}H-NMR spectra also were taken on a Unity Inova-400 spectrometer in CD_3COCD_3 at 30 °C.

3. Results and discussion

3.1. Polymerization of MMA with Pd(II)/Ni(II) acetylide complexes

All the late transition metal acetylides developed here are *trans* and are easy to prepare and soluble in common

Table 1
Polymerization of MMA with Pd(II)- or Ni(II)-based complexes

No.	Metal complexes	Conversion (%)	M_n (10^{-4})	M_w/M_n	Tacticity [a] (%)		
					rr	mr	mm
1	$Pd(PPh_3)_2(C{\equiv}CH)_2$	27	5.54	2.95	62.8	33.0	5.2
2	$Pd(PPh_3)_2(C{\equiv}CPh)_2$	50	9.20	2.52	63.2	33.7	3.1
3	$Pd(PPh_3)_2(C{\equiv}CCH_2OH)_2$	29	6.26	2.47	64.6	31.3	4.0
4	$Pd(PPh_3)_2(C{\equiv}CCH_2OOCCH_3)_2$	41	9.60	2.22	66.0	30.1	3.9
5	$Pd(PPh_3)_2(C{\equiv}CCH_2OOCPh)_2$	40	8.87	2.30	63.1	31.7	5.2
6	$Pd(PPh_3)_2(C{\equiv}CCH_2OOCPhOH-o)_2$	25	5.02	2.45	67.1	30.4	2.5
7	$Pd(PPh_3)_2Cl_2$	~0	–	–	–	–	–
8	$Ni(PPh_3)_2(C{\equiv}CPh)_2$	21	19.4	1.95	63.1	33.7	3.3
9	$Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$	23	17.9	2.10	63.0	31.3	5.7
10	$Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)Cl$	14	19.3	1.90	64.8	31.0	4.1
11	$Ni(PPh_3)_2Cl_2$	0	–	–	–	–	–
12	$Pd(Pn\text{-}Bu_3)_2(C{\equiv}CPh)_2$	~0	–	–	–	–	–
13	$Ni(Pn\text{-}Bu_3)_2(C{\equiv}CPh)_2$	~0	–	–	–	–	–

Note: Conditions: [MMA] = 6.77 mol/l, [cat] = 3.76×10^{-3} mol/l, $CHCl_3$, 5 h, 60 °C, N_2.
[a] ^{1}H-NMR, $CDCl_3$, 25 °C.

organic solvents. Moreover, they are air- and moisture-stable and can be handled with ease in open air. It is worth noticing that all the catalysts are single-component systems without any additives, obviating the trouble of preparing binary and ternary catalysts.

The polymerization of MMA was carried out in $CHCl_3$ with Pd(II) and Ni(II) acetylide or dichloride complexes at 60 °C. The results are summarized in table 1. All of the acetylide complexes with PPh_3 ligand show catalytic activities for the MMA polymerization (entries 1–6); meanwhile the P*n*-Bu_3 complexes, such as PBP (entry 10) and NBP (entry 11), show little activity under the same conditions. The difference in activity between the two kinds of complexes is probably due to the greater basicity and the σ-related donating ability of P*n*-Bu_3, which increases the density of the electron cloud of metal–carbon and decreases the reaction activity of this bond.

Alkynyl ligands bonded to palladium atom also exert influences on the catalytic activity of these complexes (entries 1–6). According to the conversion of the MMA polymerization, the palladium acetylide containing non-polar alkynyl ligand, *i.e.* C≡CPh, shows a little higher activity than that with polar ligands, *i.e.* $C{\equiv}CCH_2OOCCH_3$ and $C{\equiv}CCH_2OH$, probably due to the slight instability of the latter kind of complexes. In fact, $Pd(PPh_3)_2(C{\equiv}CH)_2$ is less stable than $Pd(PPh_3)_2(C{\equiv}CPh)_2$ [†] and shows a lower catalytic activity. Furthermore, the catalytic activities of nickel dichloride and monoalkynyl and dialkynyl complexes are compared. As shown in table 1, nickel dialkynyl complex shows a slightly higher catalytic activity than nickel monoalkynyl complex, and nickel monoalkynyl complex shows a much higher activity than nickel dichloride: $Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2 > Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)Cl \gg Ni(PPh_3)_2Cl_2$. In fact, neither the nickel dichloride nor the palladium dichloride shows catalytic activity for the present polymerization of MMA. These results indicated obviously that the presence of alkynyl ligand increases the catalytic activity of these complexes.

The central metal exhibits great influence on the catalytic behavior of the complex. In the present polymerization system, when Pd complex was used as initiator, the yield of PMMA was higher (entry 2), *i.e.* PPP gave 50% yield of PMMA. However, Ni complex gave only 25% yield of PMMA (entry 8). On the other hand, the polymer with higher number-average molecular weight was produced when Ni complex was used as an initiator.

PMMA obtained with these acetylide complexes in $CHCl_3$ at 60 °C have high molecular weights (M_n: $5.02–19.4 \times 10^4$) and syndio-rich microstructures. The microstructure of PMMA was determined by the ^{1}H-NMR spectrum of PMMA [13]. As shown in table 1, the structure variations of these acetylide complexes have little influence on the microstructure of PMMA. The syndiotactic contents (rr triad) range from 62.8% to 67.1%.

3.2. Polymerization of MMA with PPP

The polymerization of MMA with $Pd(PPh_3)_2(C{\equiv}CPh)_2$ (PPP) as an initiator was fully investigated. The influence of solvents on the catalytic activity of PPP towards MMA polymerization is shown in table 2. PPP shows relatively high catalytic activity in $CHCl_3$ and CCl_4, low activity in chlorobenzene and 1,2-dichloroethane, and little catalytic activity either in non-polarity solvents (such as toluene) or in high-polarity solvents (such as THF, DMSO), probably

[†] It is observed that PPE is unstable in air and its color changes from white to black-grey in several days accompanied by lower catalytic activity, while PPP shows no change in color or catalytic activity even after six months.

Table 2
Effect of solvents on catalytic activity of PPP in MMA polymerization

Solvent	Catalyst in polymerization system	Conversion (%)
Toluene	Decomposition [a]	0
CCl_4	No decomposition	42
Chlorobenzol	Decomposition [b]	3
$(CH_2Cl)_2$	Decomposition [b]	8
$CHCl_3$	No decomposition	49
THF	Decomposition [a]	~0
DMSO	Decomposition [a]	~0
DMF	Decomposition [a]	0
Cyclohexanone	Decomposition [a]	~0

Note: Conditions: [MMA] = 3.76 mol/l, [MMA]/[PPP] = 1000, 60 °C, 24 h, N_2.
[a] Black powder and crystal grains of PPh_3.
[b] Crystal grains of PPh_3.

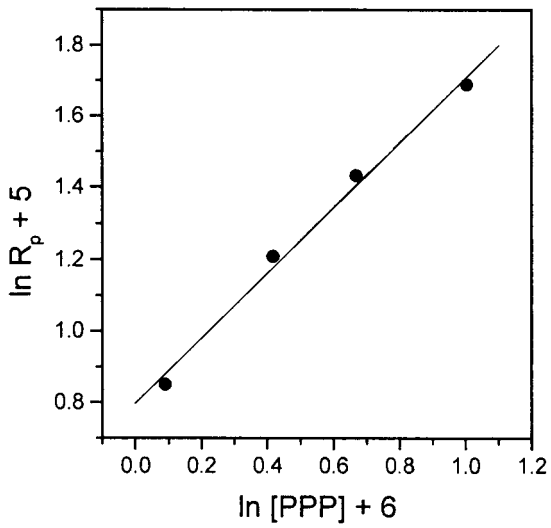

Figure 1. Plot of $\ln R_p$ *versus* $\ln$[PPP]. Conditions: [MMA] = 6.77 mol/l, $CHCl_3$, 60 °C, N_2.

owing to good solubility and stability of the complex both in $CHCl_3$ and CCl_4, and different degree of decomposition of PPP in the other solvents in the presence of MMA at polymerization temperature (as shown in table 2). Furthermore, only polymer traces were served in the absence of $CHCl_3$ or CCl_4 as in bulk polymerization; meanwhile black slurry of metallic palladium was observed. However, blank experiments show that $CHCl_3$ or CCl_4 alone cannot initiate the MMA polymerization.

The effect of catalyst concentration on the MMA polymerization is illustrated in table 3. Below 3.76 mmol/l, the conversion of polymerization, catalytic activity (here refer to kg PMMA/mol PPP) and number-average molecular weight of PMMA all increased with an increase in catalyst concentration (entries 2–5). Over 3.76 mmol/l, although the conversion increased with an increase in catalyst concentration, both the catalytic activity and the molecular weight of PMMA decreased in the same time (entry 1). The apparent polymerization rate (R_p) at different catalyst concentrations [PPP] was calculated from the conversion measured in the initial stage at constant monomer concentration [MMA] = 6.77 mol/l. Figure 1 is the plot of $\ln R_p$ *versus* $\ln$[PPP] and indicates that $\ln R_p$ is in a linear relationship with $\ln$[PPP] having a slope of approaching 1.0, *i.e.*, the polymerization reaction is of first order with respect to catalyst concentration. The influence of monomer concentration on the MMA polymerization produced is also shown in table 3. The conversion of polymerization increased with increasing monomer concentration from 1.88 mol/l to 6.77 mol/l (entries 2, 6–10). However, the further increased monomer concentration led to the decrease of polymer yield (entry 11). Figure 2 shows some curves of polymerization time *versus* $-\ln(1-c)$ at different [PPP]. From figure 2 it is clear that the polymerization reaction is of first order with respect to monomer concentration [MMA] under the tested catalyst concentration. This also means that the concentration of growing centers is approximately constant until the polymerization has proceeded for about 2 h.

Table 3
MMA polymerization catalyzed by PPP

No.	[MMA] (mol/l)	[PPP] × 10^3 (mol/l)	[MMA]/[PPP]	Conversion (%)	Catalytic activity (kg PMMA/mol PPP)	$M_n \times 10^{-4}$	M_w/M_n
1	6.77	6.77	1000	76	79.8	11.5	2.14
2	6.77	3.76	1800	68	123.1	14.1	2.98
3	6.77	2.71	2500	50	123.8	12.0	2.58
4	6.77	2.26	3000	37	109.4	11.5	2.47
5	6.77	1.69	4000	14	54.8	9.58	2.07
6	1.88	3.76	600	25	12.5	–	–
7	2.81	3.76	800	35	28.0	–	–
8	3.76	3.76	1000	43	42.7	–	–
9	4.69	3.76	1200	53	63.6	–	–
10	5.64	3.76	1500	66	99.0	–	–
11	7.51	3.76	2000	51	102.0	41.6	3.16

Note: Conditions: 10 h, 60 °C, N_2.

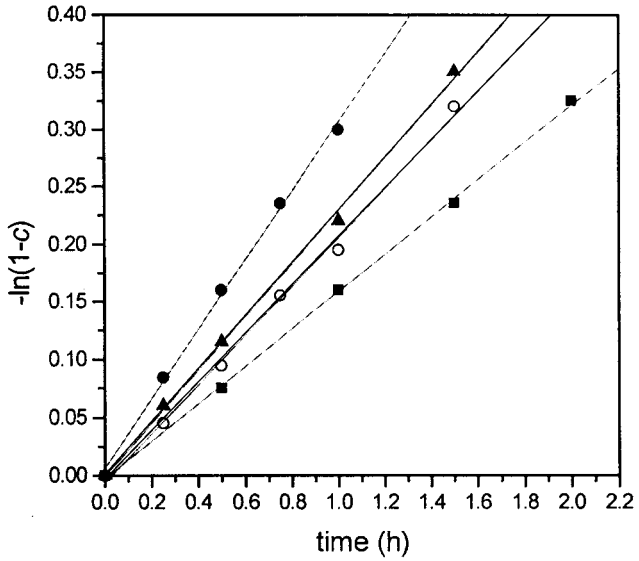

Figure. 2 Polymerization time *versus* $-\ln(1-c)$ curves at different catalyst concentration: ●, 6.77×10^{-3} mol/l; ▲, 4.28×10^{-3} mol/l; ○, 3.76×10^{-3} mol/l; ■, 2.71×10^{-3} mol/l. Conditions: same as in figure 1.

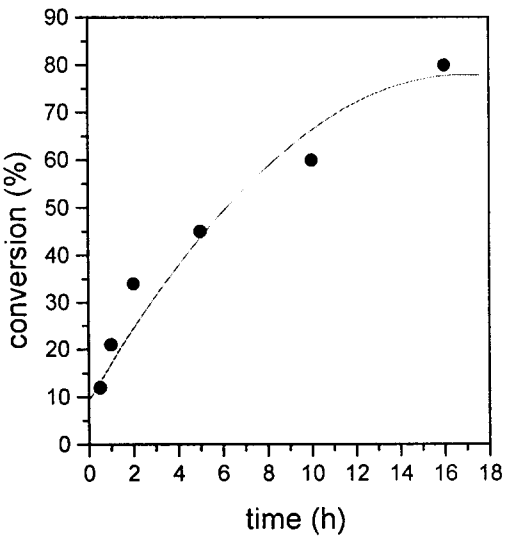

Figure 3. Polymerization of MMA with PPP in $CHCl_3$ at 60 °C. Conditions are the same as in table 4.

However, as shown in table 4 and figure 3, although the polymerization of MMA occurred without an induction period and conversion increased with increasing polymerization time, the apparent polymerization rate decreased more rapidly with a further increase in polymerization time. Table 4 also shows the number-average molecular weight and the molecular weight distribution of polymers obtained at different polymerization time. Below 10 h, the number-average molecular weight increased with an increase in time, *i.e.* when polymerization time extended from 0.5 h to 10 h, the number-average molecular weight of PMMA increased from 6.80×10^4 to 14.1×10^4. Beyond 10 h, the number-average molecular weight remained almost constant during the course of the polymerization. Also, the polydispersity (M_w/M_n) showed a slight increase, indicating the existence of chain-transfer reactions in the present polymerization system.

The present polymerization can proceed at a range of temperature from 30 to 60 °C in $CHCl_3$ (table 5), and it is very sensitive to the variation of polymerization temperature. Rising polymerization temperature caused a higher polymerization rate. As seen from table 5, the polymerization conversion rapidly increased from 8% to 68% when polymerization temperature increased from 30 to 60 °C. However, the tacticity of the polymers obtained at different temperature changed slightly. Table 5 also shows the relation between polymerization temperature and the number-average molecular weight of the polymers produced. The number-average molecular weight of PMMA decreased with an increase in polymerization temperature, indicating that side reactions are enhanced by an increase in temperature. Furthermore, figure 4 shows the plot of the apparent polymerization rate (R_p) $\{R_p = k_p[\mathrm{MMA}][\mathrm{PPP}]\}$ *versus* polymerization temperature and indicates an Arrhenius-type dependence ($k_p = A\,e^{-E_a/RT}$). Thus, the overall activation energy E_a of MMA polymerization with PPP catalyst is found to be 133.9 kJ/mol.

3.3. Polymerization mechanism

Although a detailed analysis of the intimate mechanism has to be undertaken, some experimental results are in favor of a radical pathway. As shown in tables 1 and 5,

Table 4
Effect of polymerization time on MMA polymerization with PPP

Polymerization time (h)	Conversion (%)	R_p [kg PMMA/(mol PPP·h)]	$M_n \times 10^{-4}$	M_w/M_n
0.5	12	43.24	6.80	2.42
1	21	37.84	5.29	1.97
2	34	30.63	7.10	1.94
5	45	16.22	9.20	2.52
10	60	10.81	12.0	2.52
16	80	9.01	11.8	3.04

Note: Conditions: [MMA] = 6.77 mol/l, [PPP] = 3.76×10^{-3} mol/l, $CHCl_3$, N_2.

Table 5
Effect of polymerization temperature on MMA polymerization with PPP

Polymerization temperature (°C)	Conversion (%)	$M_n \times 10^{-4}$	M_w/M_n	E_a [a] (kJ/mol)
30	8	–	–	–
40	23	13.6	1.77	133.9
50	30	12.7	2.10	–
60	68	12.0	2.52	–

Note: Conditions: [MMA] = 6.77 mol/l, [PPP] = 3.76×10^{-3} mol/l, 10 h, $CHCl_3$, N_2.
[a] Overall activation energy.

the overall activation energy of the MMA polymerization is 133.9 kJ/mol, which is much higher than that for a Ziegler–Natta catalyst system [13]. The tacticity of PMMA prepared in this work is in line with the tacticity usually reported for PMMA initiated by a free radical initiator, *i.e.* ~60–65% syndiotactic triads [14]. Moreover, although the present MMA polymerization system cannot be hindered by the incorporation of a weak radical inhibitor, *e.g.* hydroquinone, it is completely hindered by the addition of TEMPO, a strong and efficient radical scavenger. Careful experiments showed that the addition of varying amounts of hydroquinone only slightly reduced the polymer yield. For example, when 1% or 2% (referred to monomer weight) amounts of hydroquinone were added with PPP (in large excess to PPP mole), the conversion of polymerization still remained at 48% or 47% (in contrast to entry 2, table 1), respectively. However, no matter when (in the beginning or 2 h of polymerization) TEMPO (2 equiv to PPP) was added into the polymerization system, the polymerization was completely stopped. The MMA polymerization initiated by AIBN (conditions are same as in table 1), which is a classical radical initiator, was completely stopped by adding the same amount of hydroquinone or TEMPO. In addition, after an anion scavenger (MeOH, 10 vol%) was added to the polymerization at a conversion of 45%, the conversion reached 80% together with an increased molecular weight in an additional 12 h. These results indicate that the present polymerization proceeds *via* a radical mechanism.

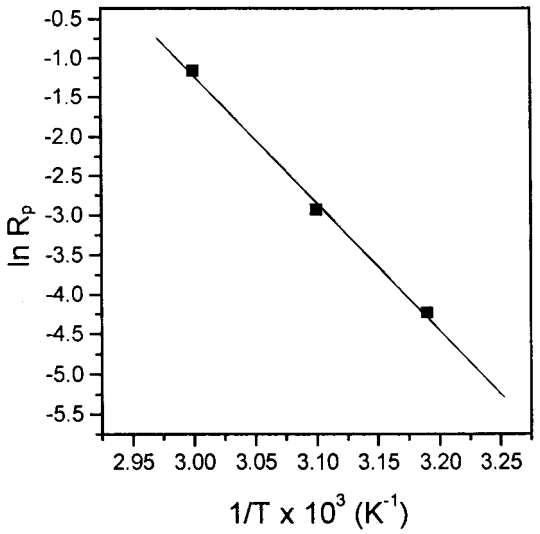

Figure 4. Arrhenius plot of the rate of polymerization (k_p) *versus* temperature. Conditions: [MMA] = 6.77 mol/l, [PPP] = 3.76×10^{-3} mol/l, $CHCl_3$, N_2.

3.4. End-group characterization

According to the mechanism provided by Sawamoto [15] for ATRP of MMA with $NiX_2(P\textit{n}\text{-}Bu_3)_2$-based catalyst system (shown in scheme 1), the resulting polymer chain contains a dormant carbon–halogen terminal, which is reversible and could homolytically be cleaved into a radical species to induce a new living radical polymerization. Our experiments have found that the palladium or nickel acetylide complexes showed rather good catalytic activities for the MMA polymerization in the presence of organic halide, such as $CHCl_3$ or CCl_4, and meanwhile showed almost no catalytic activities in the absence of $CHCl_3$ or CCl_4. These results suggest that the radical species in the present polymerization system also may be generated from the halide solvent by the similar mechanism shown in scheme 1. Since the oligomer of MMA (OMMA) was produced from the oligomerization of MMA with CCl_3Br in the presence of $Ni(P\textit{n}\text{-}Bu_3)_2(C{\equiv}CPh)_2$ (NBP), presumably for the oligomerization reaction proceeding *via* the mechanism shown in scheme 1 the chain end should be a bromine atom. Then, the oligomer should be able to initiate the polymerization of a fresh feed of MMA in the presence of a classical ATRP catalyst, $Ni(P\textit{n}\text{-}Bu_3)_2Cl_2$, instead of the role of organic halide. The experience confirms this hypothesis. It is observed that no PMMA was prepared after 8 h of polymerization, using $Ni(P\textit{n}\text{-}Bu_3)_2Cl_2$ catalyst alone in toluene at 80 °C. However, if an isolated OMMA (~5 mg) was added with $Ni(P\textit{n}\text{-}Bu_3)_2Cl_2$, 13% yield of PMMA was obtained after 8 h of polymerization in toluene at 80 °C. The experimental result demonstrates the presence of a bromine atom at the end of the OMMA.

On the other hand, as seen from figure 5, the ^{1}H-NMR spectrum of the oligomer (OMMA) shows a series of small peaks at 7.47–7.77 ppm, which could be assigned to the chemical shifts of phenyl protons of C≡CPh group (figure 4). Although these peaks are very small, repeated tests always show that there are several peaks at the same range of chemical shifts. These results indicate that methyl methacrylate oligomer may be terminated with an alkynyl ligand end, and the present polymerization also might be induced by an alkynyl radical. Further investigation focused on developing the control of the polymerization reaction together with the precise polymerization mechanism are now in progress.

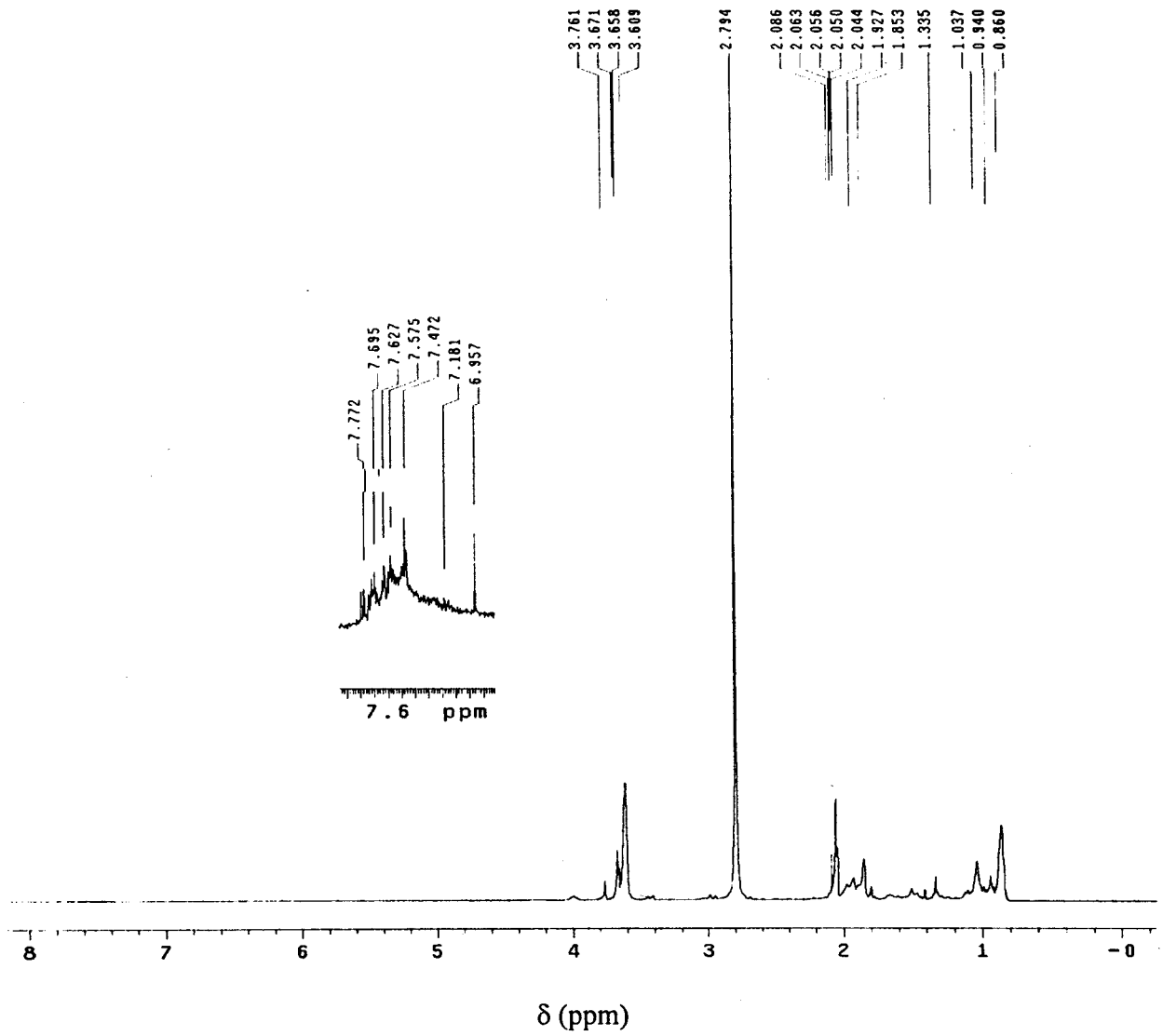

Figure 5. ^{1}H-NMR spectrum of OMMA (CD_3COCD_3, 400 MHz, 25 °C).

4. Conclusions

This paper presents a novel family of neutral, single-component, late transition metal-based MMA polymerization initiators. The catalytic behavior of these late transition metal acetylide complexes is related to the central metal, phosphine, and alkynyl ligands bonded to the metal atoms. The PMMA with high molecular weight and syndiotactic-rich microstructure was obtained with these initiators. Among them, $Pd(C{\equiv}CPh)_2(PPh_3)_2$ (PPP) showed the highest activity in $CHCl_3$ at 60 °C. The MMA polymerization by PPP was hindered by the addition of TEMPO and was assumed to proceed *via* a radical mechanism. The molecular weight distribution of the PMMA is somewhat lower than that obtained by AIBN. Although the concentration of growing centers is approximately constant in the initiating period of the polymerization ($t \leq 2$ h), and the number-average molecular weight also increased with an increase in time ($t \leq 10$ h), the control of the polymerization is poor under the test conditions. Other monomers, such as styrene and butyl acrylate, are being tested under the above-mentioned experimental conditions, and the control for these monomers is also poor. So, a deeper study of the polymerization mechanism is required and will allow a comparison of the present results with those reported for metal-mediated ATRP polymerization.

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