Catalysis Letters Vol. 90, Nos. 1–2, September 2003 (© 2003)

Neutral Pd(II) and Ni(II) acetylide initiators for polymerization of (dimethylamino)ethyl methacrylate

Sun Hongmei, Pang Xinan, Chen Mansheng, and Shen Qi*

Department of Chemistry and Chemical Engineering, Soochow University, Suzhou 215006, China

Received 8 April 2003; accepted 9 July 2003

A series of air-stable, late transition, metal-based initiators with the structures $ML_2(C\equiv CR)_2$ (M = Pd and Ni; L = PPh_3 and P*n*-Bu_3; R = Ph and CH_2OH) for the polymerization of (dimethylamino)ethyl methylate (DMAEMA) were developed. Transition metal, phosphine, alkynyl, as well as solvents exhibited significant influence on the polymerization. Among them, $Pd(C\equiv CPh)_2(PPh_3)_2$ (PPP) shows the highest activity in $CHCl_3$ for DMAEMA polymerization. The PDMAEMA obtained is a syndiotactic polymer with high number-average molecular weight (M_n) of 20.2×10^4. A free radical polymerization mechanism with some ATRP characteristics was proposed for the present polymerization.

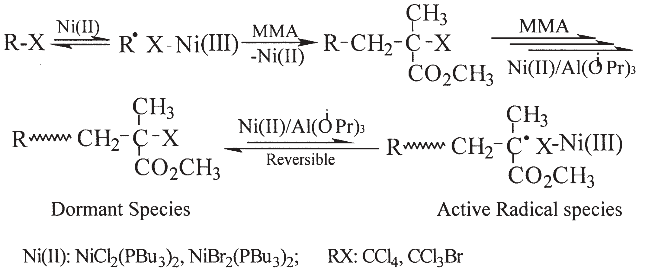
KEY WORDS: polymerization; (dimethylamino)ethyl methylate; late transition metal acetylide; initiator.

1. Introduction

For more than 40 years, early transition metal-type catalysts have received extensive attention both in industry and academia [1]. However, their strongly oxophilic nature limits them mostly to the polymerizations of nonpolar monomers, with Lewis base being a poison.

Consequently, less oxophilic catalytic systems based on late transition metals have emerged [2–4] in order to find new ways of preparing polymers or copolymers containing polar units or functionalities. The catalytic systems developed extensively in recent years can be mostly categorized into two series: one is based on Brookhart's cationic Ni(II) and Pd(II) α-diimine ligands complexes [2] and the other is based on neutral metal halide complexes, like Ni [3], Pd [4], Cu [5], Fe [6], and Ru [7] accompanied with organic halides and ligands. The former system proved to be very active and was able to copolymerize ethylene or α-olefins with methyl acrylate by an insertion–coordination mechanism [8]. In the latter system, an initiating carbon radical was generated from the C–X bond of an organic halide via the single-electron redox reaction of the metal complex (scheme 1) [3], and thus controlled or living radical polymerization of styrenic, acrylic, and methacrylic monomers was achieved. One of the features of such late transition metal-catalyzed systems may lie in possible modulation of catalytic activity by the central metals as well as the ligands so as to be suited for control of radical polymerization. So, an important but unattained subject is, therefore, developing new metals and new ligands with improved activities to define the scope of (transition) metal complexes and their ligands for this type of polymerization.

In general, transition metal to alkyl or aryl M–C σ bond is unstable at room temperature and is air and water sensitive. However, if both of the 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, the stable alkynyls can be prepared, e.g. *trans*-$(PPh_3)_2Pd(C\equiv CPh)_2$ [9]. In recent years, some transition metal acetylides were found to be active catalysts for alkynes cyclotrimerization or polymerization via a coordination/insertion mechanism [10]. We also reported the development of highly active Pd(II)- and Ni(II)-acetylide complexes of the type $(PR'_3)_2(C\equiv CR)_2$ [M = Pd, Ni; R′ = Ph_3, *n*-Bu_3; R = Ph, CH_2OH, CH_2OOCCH_3, CH_2OOCPh, $CH_2OOCPhOH$-*o*, $C\equiv CC_6H_4C\equiv CH$] for the polymerizations of polar alkynes, e.g. propargyl alcohol (OHP) [11]. Very recently, we firstly extended the study to the polymerization of monofunctional vinyl monomer and found that some of these acetylide complexes could catalyze the polymerization methyl methacrylate



Scheme 1.

---

* To whom correspondence should be addressed.
E-mail: qshen@suda.edu.cn

(MMA) via a radical mechanism with some control characteristics [12]. To the best of our knowledge, no report demonstrates the title complexes' capability in polymerization of polar monomers with polyfunctional groups, such as (dimethylamino)ethyl methacrylate (DMAEMA), which contains both ester and amido groups. Furthermore, poly (dimethylamino) ethyl methacrylate (PDMAEMA) is a hydrophilic amino-polymer that can be easily converted to a cationic polyelectrolyte by quaternization or to a polybetaine by betainization, thus can be used in the petroleum industry and for environmental protection. So, we describe here the first example of the homogeneous polymerization of DMAEMA using Pd(II)- and Ni(II)-based acetylide complexes as initiators in $CHCl_3$.

2. Experimental

2.1. Materials

All solvents were analytical grade. DMAEMA and MMA (methyl methacrylate) were dried over CaH_2 and distilled under Ar atmosphere at reduced pressure. Diethylamine was dried over CaH_2 and distilled under Ar atmosphere. $CHCl_3$ and CCl_4 were distilled over phosphorous pentoxide before use. Toluene and THF were distilled from Na/benzophenone ketyl prior to use. Other solvents were dried over activated 4 Å molecular sieves and bubbled with dry Ar for more than 15 min immediately before use. Azobis(isobutyronitrile) (AIBN) were recrystallized from 95% ethanol. 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Aldrich) was used as received. Late transition metal acetylides $Pd(PPh_3)_2(C\equiv CPh)_2$ (PPP) [9], $Pd(Pn\text{-}Bu_3)_2(C\equiv CPh)_2$ (PBP) [13], $[Pd(PPh_3)_2(C\equiv CCH_2OH)_2$ (PPO) [11a], $Ni(PPh_3)_2(C\equiv CPh)_2$ (NPP) [11b], $Ni(Pn\text{-}Bu_3)_2(C\equiv CPh)_2$ (NBP) [11b] $Pd(PPh_3)_2Cl_2$ [9], $Ni(PPh_3)_2Cl_2$ [11b], and $Ni(Pn\text{-}Bu_3)_2Cl_2$ [11b] were prepared according to the literatures.

2.2. Polymerization of DMAEMA

As a general procedure, under dry argon, the solvent $CHCl_3$ and DMAEMA were added into a dry glass ampule containing the solid catalyst in turn. Then, the sealed ampule was placed in a water bath held at the desired temperature. After a specific time, the polymerization was stopped by adding 2% HCl/ethanol. The resultant polymer was dissolved in THF, followed by precipitation in petroleum. After filtration, the sticky polymer was dried in vacuum at 30 °C for 24 h. The polymer yield was determined gravimetrically.

2.3. Characterizations

The molecular weights of PDMAEMA (M_n and M_w) and the polydispersity index (M_w/M_n) were measured on a Shimadzu gel permeation chromatograph with three Ultrastyragel columns versus polystyrene standard in THF with 1 vol% triethylamine at 25°C. ^{13}C-NMR spectra were taken on a Unity Inova-400 (400 MHz) spectrometer in CD_3COCD_3 at 25 °C, using tetramethylsilane as the internal reference.

3. Results and discussion

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

All the late transition metal acetylide complexes used here are easy to prepare and are soluble in common organic solvents. Moreover, they are air- and moisture-stable and can be handled with ease in open air [13]. It is worth noticing that all the initiators are single-component systems without any additives, obviating the trouble of preparing binary and ternary catalysts.

The polymerization of DMAEMA 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. According to the polymer yield of the MMA polymerization, all of the acetylide complexes with PPh_3 ligand are effective initiators (entries 1–4); meanwhile the $Pn\text{-}Bu_3$ complexes, such as PBP (entry 5) and NBP (entry 6), show little activity under the same conditions that are very similar to those found in the MMA polymerization [12]. The difference in catalytic activity between the two kind of complexes is probably due to the greater basicity and the related σ-donating ability of $Pn\text{-}Bu_3$, which increases the density of electron cloud of the metal–carbon bond and decreases the reaction activity of this bond [11c].

Other ancillary ligands, such as alkynyl ligands and chlorine atom, also exert influences on the catalytic properties of these complexes. For example, the palladium complex containing nonpolar alkynyl ligand, i.e. $C\equiv CPh$ shows a little higher catalytic activity than the corresponding complex containing a polar one, i.e., $C\equiv CCH_2OH$ (entries 1 and 3), probably due to the slight instability of the latter complex. In fact, it is observed that PPO is somewhat unstable and its color changes from white to yellowish brown in several weeks accompanied by a lower catalytic activity, while PPP shows no changes in color and catalytic activity even after six months. Besides, the palladium or nickel dialkynyl complexes show a higher catalytic activity than the corresponding dichlorides, i.e., $(PPh_3)_2Pd(C\equiv CPh)_2 > (PPh_3)_2PdCl_2$, indicating apparently that the presence of alkynyl ligand increases the catalytic activity of these complexes.

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

Entry	Metal complex	Yield (%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_n/M_w
1[a]	$(PPh_3)_2Pd(C{\equiv}CPh)_2$	60	16.2	27.5	1.70
2[b]	$(PPh_3)_2Pd(C{\equiv}CPh)_2$	90	20.2	39.8	1.97
3[a]	$(PPh_3)_2Pd(C{\equiv}CCH_2OH)_2$	50	13.2	21.1	1.59
4[a]	$(PPh_3)_2Ni(C{\equiv}CPh)_2$	14	18.1	29.1	1.60
5[a]	$(Pn\text{-}Bu_3)_2Pd(C{\equiv}CPh)_2$	4	/	/	/
6[a]	$(Pn\text{-}Bu_3)_2Ni(C{\equiv}CPh)_2$	5	/	/	/
7[b]	$(PPh_3)_2PdCl_2$	40	21.7	37.1	1.71
8[b]	$(PPh_3)_2NiCl_2$	6	/	/	/
9[a]	$(Pn\text{-}Bu_3)_2NiCl_2$	≈0	/	/	/

Note: Conditions: $CHCl_3$, 6 h, 60 °C, Ar.
[a][DMAEMA] = 4.5 mol/L, [PPP] = 1.5×10^{-3} mol/L.
[b][DMAEMA] = 5.0 mol/L, [PPP] = 2.0×10^{-3} mol/L.

The central metal exhibits great influence on the catalytic behavior of the complex. As shown in table 1, at the present polymerization conditions, when palladium complex was used as initiator, the yield of PDMAEMA was higher (entry 1), i.e., PPP gave 60% yield of PDMAEMA; however, nickel complex gave only 14% yield of PDMAEMA (entry 4). In the meantime, the polymer with higher number-average molecular weight was obtained when nickel complex was used as an initiator.

It is noteworthy that the solvent also shows great influence on the present polymerization. The results are summarized in table 2. For instance, when PPP was used as the initiator, the DMAEMA polymerization showed high reaction activity in chlorinated hydrocarbon, such as $CHCl_3$ and CCl_4, and relatively low activity either in nonpolarity solvents (such as toluene) or in high-polarity solvents (such as THF, DMF), probably due to good solubility and stability of PPP both in $CHCl_3$ and CCl_4 [12]. In fact, decomposition of PPP in the other solvents in the presence of DMAEMA at polymerization temperature is observed. However, blank experiments show that $CHCl_3$ or CCl_4 alone cannot initiate the DMAEMA polymerization. By the way, the influence of the amount of used solvent on the DMAEMA polymerization also has been observed. It is found that a higher monomer concentration is of benefit to an obviously higher polymer yield (in contrast to entries 1 and 2, table 1) along with a slight increase in MWDs (M_n/M_w).

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

Solvent	Catalyst in polymerization system	Yield (%)
Toluene	Decomposition[a]	8
CCl_4	No decomposition	56
$CHCl_3$	No decomposition	50
THF	Decomposition[a]	1
DMF	Decomposition[a]	8
1,4-dioxane	Decomposition[a]	11

Note: Conditions: [DMAEMA] = 3.71 mol/L, [PPP] = 1.48×10^{-3} mol/L, 60 °C 24 h, Ar.
[a]Black powder and crystal grains of PPh_3.

PDMAEMA obtained with these acetylides complexes in $CHCl_3$ at 60 °C have high molecular weights with M_n values in the range of 10^5 and syndio-rich microstructures [15]. Although the type of catalyst affects the yields and molecular weights of the obtained polymers, the structure of the polymer obtained with different palladium and nickel complexes is almost the same. According to the data of the ^{13}C-NMR spectra of these polymers, the syndiotactic contents (rr triad) range from 62.5 to 65.9%.

3.2. Polymerization mechanism

As reported in our previous literature [14], the polymerization of substituted acetylenes initiated with the same type of palladium or nickel acetylide complexes follows a coordination/insertion mechanism; polymer can be formed via the insertion of monomers into metal–carbon σ-bonds with preliminary activation at the expense of π-complex formation. However, in the present DMAEMA polymerization, although a detailed analysis of the intimate mechanism has to be undertaken, some preliminary experimental results are in favor of a radical pathway with some ATRP characteristics, which are similar to those found in the MMA polymerization [12]. As shown in table 3, although the present DMAEMA polymerization cannot be stopped 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 partly reduced the speed of the present DMAEMA polymerization. For instance, when 1 or 2% (referred to monomer weight) amounts of

Table 3
Effect of additives on catalytic activity of PPP in DMAEMA polymerization

Entry	Hydroquinone (mg)	TEMPO (mg)	CCl_3Br (μL)	[Additive]/[PPP]	Yield (%)
1	/	/	/	/	91
2	9.33	/	/	40:1	69
3	14.0	/	/	60:1	65
4	/	1.48	/	4:1	0
5[a]	/	/	/	/	26
6[b]	/	4.00	/	10:1	28
7[c]	/	/	/	/	10
8[c]	/	/	3.5	4	$\sim$100

Note: Conditions: [DMAEMA] = 5 mol/L, [PPP] = 2×10^{-3} mol/L, $CHCl_3$, 60 °C, 6 h, Ar.
[a] Reaction time: 2 h.
[b] Reaction time: 24 h, TEMPO was added after 2 h of DMAEMA polymerization.
[c] [DMAEMA]/[PPP] = 400, in bulk, 60 °C, 6 h, Ar.

hydroquinone were added with PPP (in large excess to the PPP mole) at the beginning of the polymerization, the polymer yield still remained at 69 or 65% (in contrast to entry 1, table 3), respectively. Meanwhile, no matter when (at the beginning or 2 h of polymerization) TEMPO (4 or 10 equiv. to PPP, respectively) was added into the polymerization system, the polymerization was completely stopped. By the way, the DMAEMA polymerization initiated by AIBN (conditions are the same as in table 3), which is a classical radical initiator, was completely hindered by adding the same amount of hydroquinone or TEMPO. In addition, the tacticity of PDMAEMA prepared by PPP is in line with that prepared by AIBN, i.e., ~60–65% syndiotactic triads. Besides, after an anion scavenger (MeOH, 10 vol%) was added to the polymerization system at a polymer yield of 27%, the yield could reach 70% together with an increased molecular weight in an additional 3 h. These results confirm that the present polymerization proceeds via a radical mechanism.

On the other hand, according to the mechanism provided by Sawamoto for ATRP of MMA with $NiX_2(Pn\text{-}Bu_3)_2$-based catalyst system (shown in scheme 1), the resulting polymer chain must contain a dormant carbon–halogen terminal, which is reversible and could homolytically cleave into a radical species to induce a new living radical polymerization [3]. Our experiments have tested that PPP showed especially good catalytic activity for the DMAEMA polymerization in the presence of organic halides, i.e. $CHCl_3$ and CCl_4, and almost no catalytic activity 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 a similar mechanism shown in scheme 1. Accordingly, the PDMAEMA obtained with PPP in $CHCl_3$ should have a carbon–chlorine terminal and should be able to initiate the polymerization of a fresh feed of MMA in the presence of a classical ATRP catalyst, $Ni(Pn\text{-}Bu_3)_2Cl_2$, instead of the role of organic halide, CCl_3Br or CCl_4. The experiment confirms this hypothesis. It is observed that no PMMA was obtained after 8 h of polymerization [17], using $Ni(Pn\text{-}Bu_3)_2Cl_2$ alone in toluene at 80 °C. However, if a carefully isolated PDMAEMA with low molecular weight (~10 mg) was added with $Ni(Pn\text{-}Bu_3)_2Cl_2$, 13% yield of PMMA was obtained after 8 h of polymerization in toluene at 80 °C. The experimental results demonstrate the presence of a chlorine atom at the end of the PDMAEMA chain. Consequently, these observations prompt us to test the new catalysts, i.e., PPP, with classical ATRP-cocatalysts, i.e. CCl_3Br, in place of the $CHCl_3$ solvent. As shown in table 3 (entries 7–8), PPP alone showed very low catalytic activity for the DMAEMA polymerization in bulk with a 10% yield of polymer; however, when 3.5 μL of CCl_3Br was added with PPP as an initiator at the beginning of the polymerization, the polymer yield reached 100% at the same conditions, which implied that the palladium acetylide complex might lead to a new type of catalyst for ATRP.

Furthermore, to investigate the living nature of the DMAEMA polymerization with PPP in $CHCl_3$ at 60 °C, a fresh feed of DMAEMA was added to the reaction mixture [18] when most of the initial charge of DMAEMA was consumed (ca. 85% in 12 h). After the addition, a smooth second-phase polymerization took place, and polymer yield reached 186% (>90% consumption of the add DMAEMA) in an additional 18 h, while the molecular weight (M_n) increased from 29,400 to 44,300 with MWDs ($M_w/M_n = 1.91$ and 2.26 respectively) remaining unimodal. These results suggest that PPP may be suitable for living radical polymerization of DMAEMA. Further investigations focused on developing the control of the polymerization reaction together with the precise polymerization mechanism are now in progress.

4. Conclusions

This paper presents a new series of late transition metal acetylide initiators for the polymerization of DMAEMA. The catalytic behavior of these acetylide complexes is related to central metal, phosphine, and alkynyl ligands bonded to the metal atoms. The PDMAEMA 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 with some ATRP characteristics. However, a deeper study of the polymerization mechanism together with the control of the polymerization reaction is required and will hope to find a new initiator system for the ATRP of DMAEMA.

Acknowledgments

We thank the National Natural Science Foundation of China, the Department of Education of Jiangsu Province and Key Laboratory of Organic Chemistry, Jiangsu Province, for the financial support.

References

[1] (a) G.G. Hlatky, Chem. Rev. 100 (2000) 1347. (b) K. Soga and T. Shiono, Prog. Polym. Sci. 22 (1997) 1503.

[2] (a) S.D. Ittel, L.K. Johnson and M. Brookhart, Chem. Rev. 100 (2000) 1169. (b) L.S. Boffa and B.M. Novak, Chem. Rev. 100 (2000) 1479.

[3] (a) H. Uegaki, Y. Kotani, M. Kamigaito and M. Sawamoto, Macromolecules 30 (1997) 2249. (b) H. Uegaki, Y. Kotani, M. Kamigaito and M. Sawamoto, Macromolecules 31 (1998) 6756.

[4] Ph. Lecomte, I. Drapier, Ph. Dubois, Ph. Teyssié and R. Jérôme, Macromolecules 30 (1997) 7631.

[5] (a) Y.Q. Shen, S.P. Zhu, F.Q. Zeng and R.H. Pelton, Macromolecules 33 (2000) 5427. (b) J. Queffelec, S.G. Gaynor and K. Matyjaszewski, Macromolecules 33 (2000) 8629.

[6] (a) S.M. Zhu and D.Y. Yan, Macromolecules 33 (2000) 8233. (b) K. Matyjaszewski, M. Wei, J. Xia and N.E. McDermott, Macromolecules 30 (1997) 8161.

[7] T. Nishikawa, T. Ando, M. Kamigaito and M. Sawamoto, Macromolecules 30 (1997) 2244.

[8] S. Mecking, L.K. Johnson, L. Wang and M. Brookhart, J. Am. Chem. Soc. 120 (1998) 888.

[9] M.J. Yang, K. Ding, L.J. Zhang and W.G. Chen, Synth. Met. 71 (1995) 1739.

[10] (a) Y. Kishimoto, P. Eckerle, T. Miyatake, T. Ikariya and R. Noyori, Macromolecules 29 (1996) 5054. (b) Y. Kishimoto, P. Eckerle, T. Miyatake, T. Ikariya and R. Noyori, J. Am. Chem. Soc. 116 (1994) 12131. (c) M.V. Russo, A. Furlani, M. Cuccu and G. Polzonetti, Polymer 37 (1996) 1715.

[11] (a) M.J. Yang and H.M. Sun, Polym. J. 27 (1995) 928. (b) X.W. Zhan, M.J. Yang and H.M. Sun, Catal. Lett. 70 (2000) 79. (c) X.W. Zhan, M.J. Yang and H.M. Sun, J. Mol. Catal., A: Chem. 169 (2001) 63.

[12] H.M. Sun, M.J. Yang, X.A. Pang and Q. Shen, Catal. Lett. 80 (2002) 11.

[13] H.M. Sun and M.J. Yang, Chin. J. Chem. 18 (2000) 896.

[14] (a) X.W. Zhan, M.J. Yang and H.M. Sun, Macromol. Rapid Commun. 22 (2001) 530. (b) X.W. Zhan and M.J. Yang, J. Mol. Catal., A: Chem. 169 (2001) 57.

[15] The syndiotacticity of the PDMAEMA was determined with reference to the reported triad of poly(methyl methacrylate) [16]. Signals of ^{13}C-NMR spectrum (CD_3COCD_3) at δ 17.3 and 19.2 ppm are assigned to rr and rm, respectively. The signal of isotacticity at about 20 ppm is so weak that cannot be observed in our experiment.

[16] (a) R.C. Ferugusan and D.W. Overnall, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 26 (1985) 182. (b) Q. Shen, Y.R. Wang, K.D. Zhang and Y.M. Yao, J. Polym. Sci., Part A, Polym. Chem. 40 (2002) 612.

[17] Polymerization conditions: $[MMA] = 7.8$ mol/l, $[Ni(P\textit{n}\text{-}Bu_3)_2Cl_2] = 7.8 \times 10^{-3}$ mol/l, toluene, 80 °C, 8 h.

[18] Polymerization conditions: $[DMAEMA] = 2$ mol/l, $[PPP] = 4\times 10^{-3}$ mol/l, toluene, 80 °C, $CHCl_3$.