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Sunjuk, Mahmoud

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ORIGINAL ARTICLE

γ -Diimine palladium(II) based complexes mediated polymerization of methyl methacrylate



Mahmoud Sunjuk ^a, Adnan S. Abu-Surrah ^{a,*}, Kayed A. Abu Safieh ^a,
Abdussalam K. Qaroush ^b, Feda'a M. Al-Qaisi ^c

^a Department of Chemistry, Hashemite University, P.O. Box 150459, Zarqa-13115, Jordan

^b WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching bei München, Germany

^c Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, P.O.Box 55, FIN-00014, Finland

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Abstract The synthesis of new palladium(II) complexes of the type [Pd(A–N=C–ph–C=N–A)Cl₂] (**4a–e**) (A = cyclohexyl (**a**), 2-isopropyl (**b**), pyrenyl (**c**), naphthyl (**d**), and 2,6-diisopropyl (**e**)) is described. The isolated γ -diimine ligands and their corresponding palladium(II) complexes were characterized by their physical properties, elemental analysis, ¹H NMR-, ¹³C NMR, and infrared spectroscopy. The palladium(II) complexes (**4a–e**) were employed successfully as catalysts for atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in the presence of ethyl-2-bromoisobutyrate (EBIB) as initiator at 90 °C. Polymerization with these catalyst systems afforded polymers with low molecular weight distribution (M_w/M_n) and syndio-rich atactic poly (MMA) with relatively higher [rr] diads.

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1. Introduction

Several new methods have been developed to obtain control over molecular weights, molecular weight distributions, functionalities, architectures, and well-defined compositions (Wang

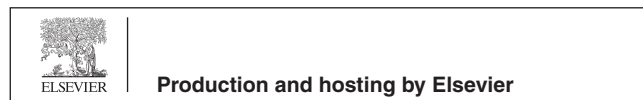
and Matyjaszewski, 1995). One of these polymerization methods is atom transfer radical polymerization (ATRP) Matyjaszewski (2012); DiLena and Matyjaszewski (2010), which has been applied to a wide range of vinyl monomers utilizing various initiators and catalyst systems.

Poly(methyl methacrylate) PMMA is an economical alternative to polycarbonate (PC) when extreme strength is not necessary. Additionally, PMMA does not contain the potentially harmful bisphenol-A subunits found in polycarbonate. It is often preferred because of its moderate properties, easy handling and processing, and low cost. Polymerization of acrylates is classically carried out using either anionic (Baskaran, 1997), radical (Matyjaszewski and Xia Chem,

* Corresponding author. Tel.: +962 795573544.

E-mail address: asurrah@hu.edu.jo (A.S. Abu-Surrah).

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2001) or group transfer polymerization (GTP) Hertler et al. (1984), but recently late transition metal complex based polymerization methods, including ATRP (atom transfer radical polymerization) (Matyjaszewski and Xia Chem, 2001) and (methylaluminoxane) MAO activated metal complexes, have also been developed, for example, for acrylates (Kim and Hwang, 2003; Castro and Lankinen, 2005).

ATRP has tolerance toward a wide variety of functional groups in the monomer and has been applied successfully for the preparation of well-defined polymers such as styrene, substituted styrenes (Turner et al., 2012; Mukumoto et al., 2012; Qiu and Matyjaszewski, 1997), (meth)acrylate Mendonca et al. (2011); Abreu et al. (2012); Levere et al. (2012); Moineau et al. (1999), and acrylonitrile (Yu, 2013; Matyjaszewski et al., 1997). As catalysts, ATRP systems use Ru (De Clerg and Verpoort, 2002; Nishikawa et al., 1997), Rh (Percec et al., 1996), Ni (Granel et al., 1996), Pd (Lecomte et al., 1997), Co (Normen et al., 2002), and Fe (Ando et al., 1997; Gibson et al., 2002), transition metals in conjunction with suitable ligands such as substituted and unsubstituted bipyridines, phosphorus-containing ligands, and multidentate amines (Matyjaszewski and Xia, 2001).

Transition metal complexes containing sterically demanding α -diimine ligands have been successfully employed in a number of catalytic reactions; including polymerization of alkenes (Brookhart et al., 1995; Schmid et al., 2001), polymerization of polar monomers (Heinemann et al., 1999), alkyne cyclotrimerization (Van der Poel et al., 1981), enantioselective 1,3-dipolar cycloaddition reaction (Saito et al., 2004) and borylation of vinylarenes (Geier et al., 2006).

The coordination chemistry of β -diimine ligands with palladium and nickel has also been reported (Domin et al., 2007; Feldman et al., 1997) and compared with the corresponding α -diimine analogs (Cope-Eatough et al., 2003). The catalytic behavior of some β -diimine zinc catalysts toward alternating copolymerization of CO₂ and epoxides was also investigated (Cheng et al., 2001). On the other hand, few investigations have lately focused on the coordination chemistry of γ -diimine-based ligands that could act as bidentate ligands forming a 7-membered ring around the metal center (Chitanda et al., 2008; Abu-Surrah et al., 2008).

Recently, we reported the implementation of pentacoordinated iron(II) complexes with 2,6-bis[(imino)ethyl]pyridine bearing cyclic aliphatic and aromatic terminal groups, as catalysts for atom transfer radical polymerization of *tert*-butyl acrylate (*t*BA) and methyl methacrylate (MMA). Polymerization with these catalysts *via* ATRP afforded polymers with very low molecular weight distribution (M_w/M_n) and syndiorich atactic poly(*t*BA) and poly(MMA) with relatively higher [rr] diads than those produced by the methylaluminoxane (MAO) activated 2,6-bis[(imino)ethyl]pyridine iron(II)-based catalyst systems (Abu-Surrah et al., 2011).

We now report on the synthesis and characterization of new palladium(II) complexes containing γ -diimine bidentate nitrogen ligands that are based on cyclohexyl, isopropyl, pyrenyl, naphthyl, and 2,6-diisopropyl as auxiliary ligands and their application as catalyst systems mediated atom transfer radical polymerization of methyl methacrylate. To the best of our knowledge this is the first report about the utilization of diimine palladium(II) based ATRP catalyst system for polymerization of acrylate monomers.

2. Experimental section

2.1. Materials

All reactions were carried out under dry nitrogen by using standard Schlenk tube techniques. The ligands **3a**, **b**, **d** were prepared as described previously by us (Abu-Surrah et al., 2008). The complex [Pd(NCPh)₂Cl₂] was prepared according to a literature procedure (Doyle et al., 1960). MMA was purchased from Fluka and used without further purification. Ethyl 2-bromoisobutyrate ((CH₃)₂CBrCO₂Et) was dried under molecular sieves. All other reagents were used as received.

2.2. Physical measurements

Elemental analyses were performed using a EURO EA 3000 instrument. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker spectrometer operating at 300 MHz using CDCl₃ as a solvent with TMS as an internal standard. Infrared spectra (KBr pellets) were measured on a Nicolet-Magna-IR 560 Spectrophotometer. Melting points were measured by a Stuart Scientific melting apparatus (uncorrected \pm 0.1 °C).

Molar masses and molar mass distributions were determined with a Waters 515 HPLC pump GPC with Styragel columns HR2, HR4 and HR6 having a UV detector Waters 2487 and a refractive index detector Waters 2410, in THF at 35 °C using polystyrene standards. Thermal gravimetric analysis was performed on a NETZSCH STA 409 PC LUX instrument (heating rate 10 K/min.).

2.3. Synthesis of ligands **3c** and **3e**

2.3.1. *N,N'*-bis(pyrenyl)-1,2-phenyldiimine (BPPD) **3c**

A solution of 1,2-phenylendicarboxylaldehyde (**1**) (5.00 g; 0.037 mol) in ethanol (40 mL) was added to a solution of the amine (**2c**) (0.086 mol) in ethanol (40 mL) with continuous stirring. The mixture was stirred at room temperature for 3 h, during which, a white precipitate was formed. The product was filtered, washed with ethanol (4 \times 15 mL) and dried in vacuum.

Yield: 13.8 g (70%). – Color: olive-green. – Mp 186 °C. – IR (KBr pellet, cm⁻¹): ν (C=N), 1666 (m). – ¹H NMR (CDCl₃): δ = 8.90 (s, 2H, HC=N). – ¹³C NMR (CDCl₃): δ = 161.8 (C=N). – C₄₀H₂₄N₂: calcd. C, 90.2; H, 4.54; N 5.26%; found C, 89.65; H, 4.67; N, 5.09%.

2.3.2. *N,N'*-bis(2,6-diisopropylphenyl)-1,2-phenyldiimine (BDPD) **3e**

Compound **3e** was prepared following the above procedure described for **3c**. A solution of 1,2-phenylendicarboxylaldehyde (**1**) (5.00 g; 0.037 mol) in ethanol (40 mL) was allowed to react with a solution of amine (**2e**) (0.086 mol) in ethanol (40 mL).

Yield: 13.9 g (83%). – Color: yellowish. – Mp 184 °C. – IR (KBr pellet, cm⁻¹): ν (C=N), 1633 (m). – ¹H NMR (CDCl₃): δ = 8.78 (s, 2H, HC=N). – ¹³C NMR (CDCl₃): δ = 161.5 (C=N). – C₃₂H₄₀N₂: calcd. C, 84.91; H, 8.91; N, 6.19%; found C, 84.81; H, 8.53; N, 5.99%.

2.4. Synthesis of complexes 4a–e

2.4.1. General procedure

To a filtered solution of $[\text{Pd}(\text{NCPH})_2\text{Cl}_2]$ (0.5 g, 1.30 mmol) in acetone (50 mL) was added with continuous stirring at room temperature a filtered solution of the desired ligand (**3a–e**) (1.56 mmol) in acetone (50 mL). Upon addition, a precipitate was formed. Stirring was continued for 12 h, and the compound was filtered, washed with acetone (2×5 mL), Et_2O (2×10 mL) and dried in vacuum.

2.4.2. $[\text{Pd}\{N,N'\text{-bis(cyclohexyl)-1,2-phenyldiimine}\}\text{Cl}_2]$, $[(\text{BCPD})\text{PdCl}_2]$ **4a**

Yield: 0.60 (97%). – Color: orange. – Mp (dec): 174 °C. – IR (KBr pellet, cm^{-1}): $\nu(\text{C}=\text{N})$, 1637 (m). – ^1H NMR (CDCl_3): $\delta = 9.08$ (s, 2H, $\text{HC}=\text{N}$). – ^{13}C NMR (CDCl_3): $\delta = 165.0$ (C=N). – $\text{C}_{20}\text{H}_{28}\text{N}_2\text{PdCl}_2 \cdot 1.5 \text{H}_2\text{O}$: calcd. C, 47.97; H, 6.24; N 5.59%; found: C, 48.32; H, 5.88; N, 5.37%.

2.4.3. $[\text{Pd}\{N,N'\text{-bis(2-isopropyl)-1,2-phenyldiimine}\}\text{Cl}_2]$, $[(\text{BipPD})\text{PdCl}_2]$ **4b**

Yield: 0.61 (86%). – Color: red. – Mp (dec): 206 °C. – IR (KBr pellet, cm^{-1}): $\nu(\text{C}=\text{N})$, 1599 (m). – ^1H NMR (CDCl_3): $\delta = 9.13$ (s, 2H, $\text{HC}=\text{N}$). – ^{13}C NMR (CDCl_3): $\delta = 165.7$ (C=N). – $\text{C}_{26}\text{H}_{28}\text{N}_2\text{PdCl}_2$: calcd. C, 57.21; H, 5.17; N, 5.13%; found: C, 57.28; H, 4.87; N, 5.16%.

2.4.4. $[\text{Pd}\{N,N'\text{-bis(pyrenyl)-1,2-phenyldiimine}\}\text{Cl}_2]$, $[(\text{BPPD})\text{PdCl}_2]$ **4c**

Yield: 0.89 (96%). – Color: dark-red. – Mp (dec): 232 °C. – IR (KBr pellet, cm^{-1}): $\nu(\text{C}=\text{N})$, 1631 (m). – ^1H NMR (CDCl_3):

$\delta = 9.20$ (s, 2H, $\text{HC}=\text{N}$). – ^{13}C NMR (CDCl_3): $\delta = 167.8$ (C=N). – $\text{C}_{40}\text{H}_{24}\text{N}_2\text{PdCl}_2$: calcd. C, 67.67; H, 3.41; N, 3.95%; found: C, 67.32; H, 3.35; N, 4.28%.

2.4.5. $[\text{Pd}\{N,N'\text{-bis(naphthyl)-1,2-phenyldiimine}\}\text{Cl}_2]$, $[(\text{BNPD})\text{PdCl}_2]$ **4d**

Yield: 0.38 (52%). – Color: dark-red. – Mp (dec.): 260 °C. – IR (KBr pellet, cm^{-1}): $\nu(\text{C}=\text{N})$, 1597 (m). – ^1H NMR (CDCl_3): $\delta = 9.10$ (s, 2H, $\text{HC}=\text{N}$). – ^{13}C NMR (CDCl_3): $\delta = 166.4$ (C=N). – $\text{C}_{28}\text{H}_{20}\text{N}_2\text{PdCl}_2 \cdot \text{H}_2\text{O}$: calcd. C, 58.0; H, 3.82; N, 4.83%; found: C, 58.35; H, 3.46; N, 4.27%.

2.4.6. $[\text{Pd}\{N,N'\text{-bis(2,6-diisopropylphenyl)-1,2-phenyldiimine}\}\text{Cl}_2]$, $[(\text{BDiPPD})\text{PdCl}_2]$ **4e**

Yield: 0.54 (66%). – Color: orange. – Mp (dec): 120 °C. – IR (KBr pellet, cm^{-1}): $\nu(\text{C}=\text{N})$, 1607 (m). – ^1H NMR (CDCl_3): $\delta = 9.54$ (s, 2H, $\text{HC}=\text{N}$). – ^{13}C NMR (CDCl_3): $\delta = 163.4$ (C=N). – $\text{C}_{32}\text{H}_{40}\text{N}_2\text{PdCl}_2$: calcd. C, 61.01; H, 6.39; N, 4.45%; found: C, 61.36; H, 6.18; N, 4.59%.

2.5. Polymerization experiments

Polymerization of methyl methacrylate was carried out under dry nitrogen in a dried Schlenk tube equipped with a magnetic stirring bar. The tube was charged with the required amount of monomer, initiator, and catalyst, sealed with a rubber septum, and degassed to remove oxygen (Table 1). Degassed methyl methacrylate monomer and degassed solvents were added with a nitrogen-purged syringe, and the tube was degassed and back-filled with nitrogen three times. The solution was stirred for 5 min. Finally, immediately after the initiator was added

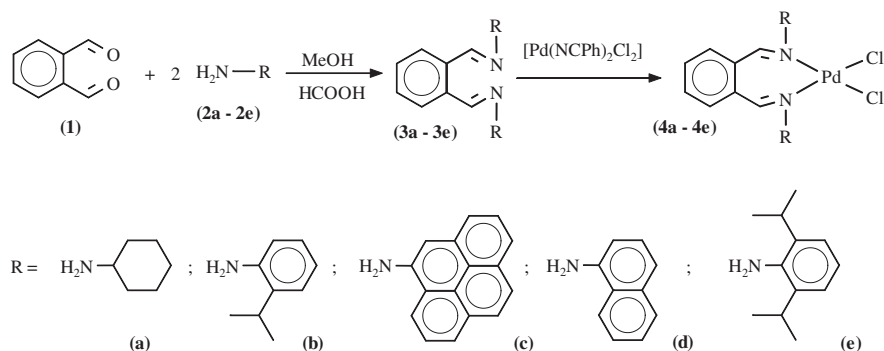
Table 1 Polymerization results of methyl methacrylate.^a

Entry	Complex	Cat. code	Time (hr)	$M_w \times 10^{3b}$	M_w/M_n^b	Conversion (%)
1	$[(\text{BDiPPD})\text{PdCl}_2]$	4e	24	-n.d. ^c	-n.d. ^c	22.3
2	$[(\text{BDiPPD})\text{PdCl}_2]$	4e	48	-n.d. ^c	-n.d. ^c	51.1
3	$[(\text{BDiPPD})\text{PdCl}_2]$	4e	54	144.7	1.62	62.0
4	$[(\text{BDiPPD})\text{PdCl}_2]$	4e	72	333.7	1.84	35.6
5	$[(\text{BDiPPD})\text{PdCl}_2]$	4e	72	147.9	1.66	74.5
6	$[(\text{BCPD})\text{PdCl}_2]$	4a	72	274.8	1.36	26.6
7	$[(\text{BNPD})\text{PdCl}_2]$	4d	72	333.1	1.44	18.1
8	$[(\text{BPPD})\text{PdCl}_2]$	4c	72	159.1	1.72	6.4

^a Polymerization conditions: $[\text{Cat.}]:[\text{In}] = 37$ (entry 5, molar ratio = 1:10); polymerization temperature = 90 °C; $[\text{monomer}]:[\text{initiator}] = 46:1$; solvent, toluene (30 mL).

^b Determined by GPC relative to polystyrene standards.

^c n.d. not determined.

**Scheme 1** Synthesis of the bidentate γ -diimine ligands (**3a–e**) and their corresponding palladium(II) complexes (**4a–e**).

via a nitrogen-purged syringe, the tube was immersed in an oil bath preheated to the desired temperature. After a given time, the reaction was stopped and the reaction mixture was cooled to room temperature and diluted with tetrahydrofuran (THF). The obtained polymer solution was passed over basic alumina to remove the catalyst, and the polymer was precipitated with an excess amount of methanol. The dried product was characterized by NMR, DSC, and GPC techniques.

3. Results and discussion

3.1. Ligand synthesis

The condensation reaction of the commercially available 1,2-phenylendicarboxylaldehyde (**1**) with about two equivalents of the desired amine in MeOH or EtOH at 25 °C afforded the bidentate γ -diimine ligands (**3a–e**) (Scheme 1).

The presence of a medium to strong peak in the range between 1618 and 1666 cm^{-1} ($\nu(\text{C}=\text{N})$) in the IR-spectra of the ligands and the disappearance of the peak due to the carbonyl group of the starting material indicate the formation of the diimine ligands.

The ^1H NMR spectra of the ligands showed a singlet resonance at about 8.8 ppm, attributed to the imine proton ($\text{HC}=\text{N}$) indicating the formation of the imine ligands. The ^{13}C -NMR spectrum of the diimines exhibits a singlet signals at around 162 ppm which can be assigned to the imine ($\text{C}=\text{N}$).

3.2. Complex synthesis

The synthesis of the complexes is shown in Scheme 1. The palladium(II) dihalide complexes bearing the γ -diimines (**4a–e**) were prepared in a moderate to high yield by treating the complex $\text{Pd}(\text{NCPH})_2\text{Cl}_2$ with the corresponding ligands in acetone at room temperature. The identity of the complexes was confirmed by elemental analysis, IR-, ^1H NMR, and ^{13}C NMR spectroscopy. The γ -diimine-based palladium(II) complexes showed good solubility in organic solvents such as chloroform (CHCl_3) and tetrahydrofuran (THF) which could be due to the higher flexibility of these complexes as the carbon atoms in the γ -diimines were part of a seven-membered ring.

Elemental analysis of the complexes (**4a–e**) confirms their purity and showed that the metal to ligand ratio in the dichloride complexes is 1:1 which indicates that the ligands act in a bidentate fashion. IR-analyses of the complexes confirm the presence of the ligands. A slight shift of the peak due to the imine bond ($\nu(\text{C}=\text{N})$) was observed in the range (1597–1637 cm^{-1}) indicating complexation of the ligands with palladium (Kettunen et al., 2004).

The solution behavior of the complexes was determined by NMR spectroscopy in CDCl_3 at room temperature. The ^1H NMR spectra of the complexes bear no unusual features, with a characteristic singlet resonance of the proton of the imine ($\text{HC}=\text{N}$) moiety in the range 9.08–9.54 ppm. This signal is shifted compared with that for the free ligands ($\delta(\text{HC}=\text{N})$ = about 8.80 ppm) indicating the coordination with palladium (Abu-Surrah et al., 2002). The complexation was also confirmed by ^{13}C -NMR; a shift for the carbon atom of the imine $\text{C}=\text{N}$ of the free ligand (~ 162 ppm) was observed upon complexation ($\delta(\text{C}=\text{N})$ = 163–168 ppm) (Lappalainen et al., 2005).

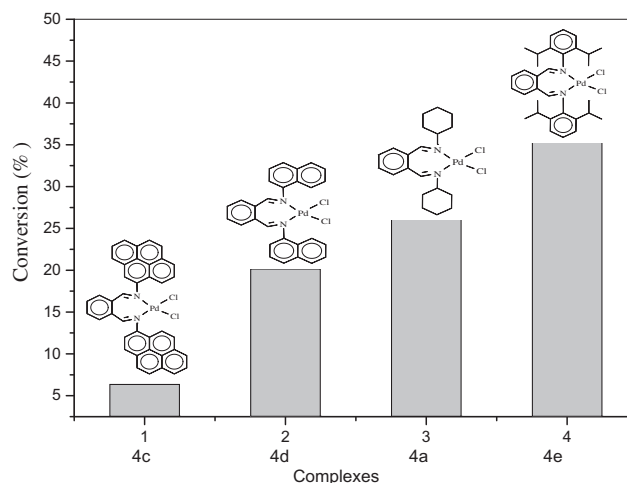


Figure 1 Dependence of monomer conversion on catalyst structure in solution polymerization of MMA at 90 °C in toluene.

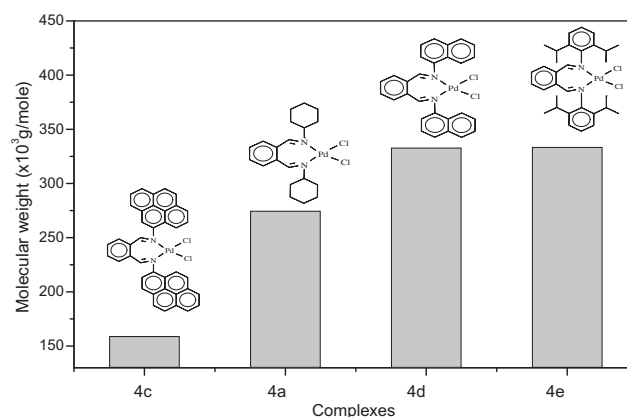


Figure 2 Dependence of molecular weight on monomer conversion in solution polymerization of MMA at 90 °C in toluene.

3.3. Polymerization experiments

Methyl methacrylate was successfully polymerized by the atom transfer radical technique using the γ -diimine based palladium(II) complexes (**4a**, **4c–e**). The influence of ligand structure, catalyst/initiator ratio, and polymerization time was explored.

The polymerization reactions were carried out at 90 °C in toluene at different polymerization times with a ratio of $[\text{monomer}]:[\text{initiator}]:[\text{cat.}] = 46:37:1$. It has been previously reported that the reaction occurred rapidly at 90 °C (Matyjaszewski et al., 1998). A relatively low catalyst/initiator molar ratio was used in order to reduce catalyst contamination to the polymers. All complexes produced PMMA polymers with relatively low molecular weight distributions as low as 1.36, in particular for complex **4a** (Table 1, entry 6).

The presence of the bulky aromatic pyrenyl terminal groups (complex **4c**) led to a decrease in both the monomer conversion and the molar mass of PMMA (Table 1, entry 8, 159.1×10^3 g/mole, Figs. 1 and 2). Under similar polymerization conditions, after 72 h, complex **4e**, which contain aliphatic substituents on

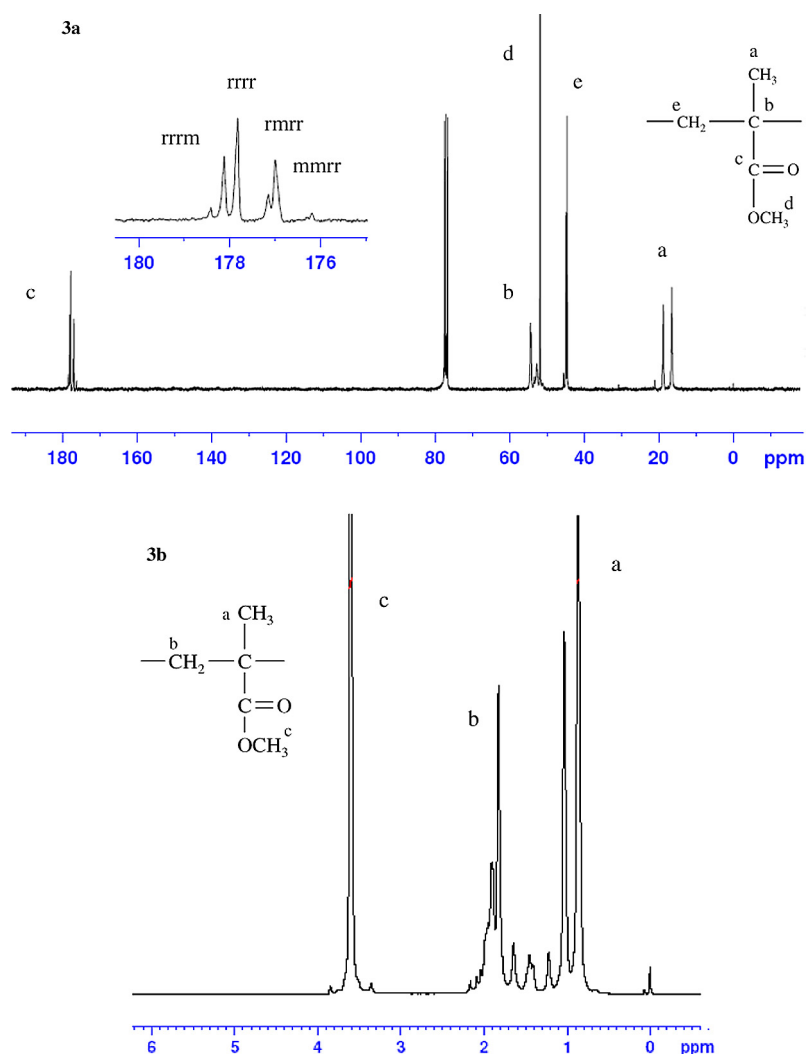


Figure 3 ^{13}C -NMR (3a) and ^1H -NMR (3b) spectra of PMMA obtained by the catalyst system $4\text{e}/(\text{CH}_3)_2\text{CBrCO}_2\text{C}_2\text{H}_5$.

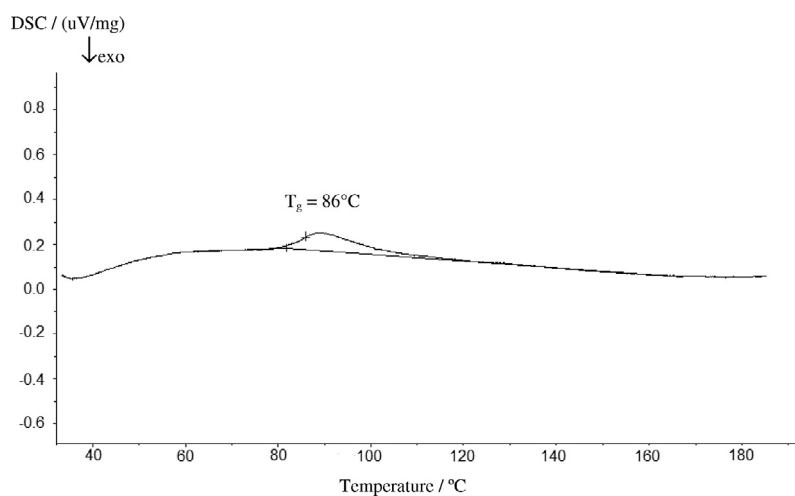


Figure 4 DSC trace of as-prepared film of PMMA obtained by the catalyst system $4\text{e}/(\text{CH}_3)_2\text{CBrCO}_2\text{C}_2\text{H}_5$.

the phenyl groups of the ligand, gave the highest monomer conversion and PMMA molar mass (Table 1, entry 4). A similar effect for the steric hindrance has also been observed in

coordination polymerization utilizing bis(imino)pyridine iron(II)-catalyzed polymerization of ethylene (Small et al., 1998) and copper-based ATRP (Xia et al., 1999).

Table 1 shows that increasing the initiator/Cat. molar ratio also has an influence on the monomer conversion. The highest conversion was reached with 1:10 M ratio (Table 1, entry 5) above that, a decrease in activity was observed. This behavior could be due to a possible interaction between the polar initiator and the catalyst center. This relative intolerance of palladium(II) complexes toward functional moieties was previously reported (Abu-Surrah and Rieger, 1996).

Polymerization experiments of MMA with complex 4e at different catalyst/initiator molar ratio at 90 °C in toluene for 72 h polymerization time indicate that time has a direct influence on the catalysts' activity (Table 1, entries 1–4), however, a drop in the monomer conversion was observed after 54 h (Table 1, entry 4).

The ¹³C-NMR spectrum of a typical PMMA polymer is displayed in Fig. 3a. Syndiotacticity of the poly (MMA) was determined with reference to the reported triad and pentad assignments (Yasuda et al., 1993). Due to the α -methyl group in MMA higher syndiotacticity values were reached (Rodríguez-Delgado et al., 2004). Signals of ¹³C-NMR at δ 178.1, 177.8, and 176.9 ppm are assigned to rrrm, rrrr, and rmrr, respectively (Fig. 3a). The ratio of these signals, 29:45:26, corresponds to a syndio-rich atactic polymer (Soga et al., 1994). Similar results have been reported with metallocene catalysts (Collins and Ward, 1992). The ¹H-NMR spectrum (Fig. 3b) shows a large absorption of the main-chain PMMA units (3.58 ppm for the ester methyl). In addition, a small signal (3.82 ppm) near the main-chain unit was observed, which can be attributed to the ester methyl protons adjacent to the bromine atom at the ω -end.

Glass transition temperature (T_g) of the isolated polymers measured by DSC was about 86 °C (Fig. 4) which indicates that the material is a transparent amorphous thermoplastic. In addition, it is close to that produced by the penta coordinated 2,6-bis[(imino)ethyl]pyridineiron(II) complexes (108 °C), which confirm that these catalyst systems also produce a syndio-rich atactic polymer (Soga et al., 1994).

4. Conclusion

New γ -diimine based palladium(II) complexes bearing various aromatic and cycloaliphatic terminal groups were prepared and characterized. The complexes were employed successfully as catalyst based systems for the polymerization of methyl methacrylate via Atom Transfer Radical Polymerization (ATRP). Increasing the bulkiness of the terminal groups on the ligand led to a decrease in the catalyst activity. The molar mass of the polymer increased by both longer polymerization time and higher initiator/catalyst molar ratio.

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