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Polymerization of vinyl monomers via MAO activated iron(II) dichloro complexes bearing bis(imino)pyridine-, quinolinaldimine- and thiophenaldimine-based tridentate nitrogen ligands

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Abstract

A series of iron(II) complexes (**4a–d**, **10**, and **11**) bearing 2,6-bis[(imino)ethyl]pyridine-(**3a–d**), quinolinaldimine-(**8**) and thiophenaldimine-(**9**) based ligands were disclosed as active complexes for the polymerization of *tert*-butylacrylate (*t*-BA). After activation with methyl aluminoxane (MAO), the complexes showed moderate to high polymerization activities and produced high molar mass polymers. In addition, the catalyst system **4d**/MAO was examined for the polymerization of methyl methacrylate (MMA) and *n*-vinylcarbazole (NVC). The influence of MAO/Cat. molar ratio, polymerization time, and monomer concentration on the polymerization reaction of methyl methacrylate was explored.

In the polymerization of *tert*-butylacrylate with 2,6-bis[(imino)ethyl]pyridine iron(II)-based catalysts, bulky terminal aliphatic substituents have a favorable influence on the polymerization activity compared to the aromatic ones. This catalyst system was also more active than the quinolinaldimine-, (**10**) and thiophenaldimine-, (**11**) based catalysts.

Keywords: Polymerization; Catalysis; Acrylate; *n*-Vinylcarbazole; Iron(II) complexes; Nitrogen tridentate ligands

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1. Introduction

In early 1970s, $(bipy)_2Fe(C_2H_5)_2$ was studied as a catalyst for the homo polymerization of polar monomers such as acrylonitrile, methyl vinyl ketone and methyl methacrylate [1,2]. However, until the middle of 1990s only few reports were introduced about utilizing late transition metal based complexes as catalyst precursors for homo- and copolymerization of 1-olefins and ethylene [3]. This is probably because these catalysts generally exhibit reduced activities for olefin polymerization and favor β-hydride elimination, which efficiently competes with the chain growth resulting in the formation of oligomers [4–6]. Recently, late transition metal complexes have attracted increasing attention [7–9], especially after the reports of Brookhart and Gibson about new Fe(II)-based complexes

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containing 2,6-bis(imino)pyridyl ligands as efficient catalyst precursors for ethylene polymerization. After MAO activation these complexes are highly active and produce strictly linear polyethylene (PE) [10,11]. We also reported on highly active 2,6-bis(arylimino)pyridine iron(II)- and cobalt(II)-based ethylene polymerization catalysts which lack the *ortho* alkyl substituents on the aryl groups [12]. Modifications of the steric bulkiness of the aromatic groups in the tridentate ligands influenced not only the catalytic activity but also molecular weight and the microstructure of the resulted material. Therefore, there is still a great interest to discover and develop new families of polymerization catalysts that can allow further control of the polymer microstructure, material properties and if possible, capable to polymerize polar vinylic monomers.

The recent development of late transition metal catalysts [8] opens an interesting platform for the polymerization of functionalized monomers, since late transition metals are less oxophilic than early transition metals, and are therefore supposed to be more tolerant toward Lewis bases [3]. For example, neutral palladium(II) complexes containing 2-iminopyrrole ligands are reported to homopolymerize methylacrylate [13] and diimine-based palladium(II) complexes were utilized as catalysts for copolymerization of ethylene and propylene with methylacrylate and *t*-BA [14].

Polymerization of acrylates is classically carried out using either anionic [15], radical [16] or group transfer polymerization (GTP) [17], but recently late transition metal complex based polymerization methods, including atom transfer radical polymerization (ATRP) [18] and MAO activated metal complexes, have also been developed [19,20]. Although the actual mechanism for MAO activated late transition metal complex assisted polymerization of acrylate monomers is still unclear (ionic vs. radical), the advantage of those systems is that they function under mild polymerization conditions with low metal complex concentrations, and the produced polymers exhibit substantial high molar masses with controlled molar mass distributions.

As an augmentation to our studies upon both the coordination chemistry of heteroatom-containing ligands [12,21–23] and their catalytic application [24], we now report the synthesis of new pentacoordinated iron(II) complexes with 2,6-bis[(imino)ethyl]pyridine-, quinolinaldimine- and thiophenaldimine-Schiff base ligands. The complexes, after activation with MAO, were evaluated as catalysts for polymerization of *tert*-butyl acrylate (*t*-BA), methyl methacrylate (MMA) and *n*-vinyl carbazole (NVC). The intention of our study is to introduce the transition metal–olefin catalyzed polymerization know-how to polar monomers in order to control their polymerization by using mild reaction conditions.

2. Experimental section

2.1. General

All reactions were carried out under dry nitrogen using standard Schlenk techniques. The synthesis of 2,6-bis[(1-phenylimino)ethyl]pyridine (BPhEP, **3a**), 2,6-bis[1-(2-benzylphenylimino)ethyl]pyridine (BBzEP, **3c**), 2,6-bis[(1-(*cis*)-myrtanylimino)ethyl]-pyridine (BMyEP, **3d**), 2,6-bis[(1-phenylimino)ethyl]pyridineiron (II) chloride (**4a**), 2,6-bis[1-(2-benzylphenylimino)ethyl]pyridineiron(II) chloride (**4c**), and 2,6-bis[1-(*cis*-myrtanylimino)ethyl]pyridineiron(II) chloride (**4d**) have been reported earlier by us [12]. Hydrocarbon solvents were purified by refluxing over $LiAlH_4$ followed by distillation under nitrogen.

Elemental analyses were performed at the Hashemite University, (EURO EA 3000 instrument). ^{1}H- and ^{13}C-NMR spectra ($CDCl_3$) were recorded on a Bruker AMX 500 soectrometer or a Varian Gemini 200 spectrometer. Infrared spectra were measured on a Nicolet-Magna-IR 560 Spectrophotometer. Molecular weight and molecular weight distributions were measured by Gel Permeation Chromatography (GPC) relative to polystyrene standards. Thermal gravimetric analysis was performed on *a*NETZSCH STA 409 PC LUXX instrument (heating rate 10 K/min).

2.2. Synthesis of ligands

2.2.1. 2,6-Bis[1-(2-isopropylphenylimino)ethyl] pyridine (BiPEP, 3b)

A solution of 2,6-diacetylpyridine (**1**) (0.4 g, 2.45 mmol) in methanol (25 ml) was added to a solution of 2-isopropylaniline (**2b**) (0.8 ml, 7.36 mmol) in the same solvent (25 ml) and three drops of (97%) formic acid. The solution was stirred for three days, during which a yellowish powder was formed which was filtered, washed with cold methanol (4 × 10 ml) and dried in vacuum. Yield: 0.40 g, 41%, m.p. = 122 °C; IR (KBr, cm^{-1}: 1643 m (C=N)); EA: Found: C, 81.71%; H, 8.21%; N, 10.71%. Calculated: $C_{27}H_{31}N_3$: C, 81.57%; H, 7.86%; N, 10.57%.

2.2.2. N′-(Quinoline-2-methylene)benzene-1,2-diamine (QMB, 8)

A solution of quinoline-2-carboxyaldehyde (**6**) (0.35 g, 2.23 mmol) dissolved in 25 ml of ethanol was mixed with a solution of 1,2-diaminobenzene (**5**) (0.219 g, 2.024 mmol) in the same solvent (25 ml) in the presence of a catalytic amount of formic acid (1 drop). The solution was refluxed for 1 h and then stirred for 3 days, during which, a brown precipitate was formed. The product was filtered, washed with cold ethanol (2 × 20 ml), and dried in vacuum. Yield: 0.31 g, 62%, m.p. = 208 °C; IR (KBr, cm^{-1}: 1638 m (C=N)); EA; Found: C, 73.21%; H, 5.30%; N, 16.56%. Calculated: $C_{16}H_{13}N_3$. H_2O: C, 72.43%; H, 5.69%; N, 15.84%.

2.2.3. N′-(Thiophene-2-methylene)benzene-1,2-diamine (TMB, 9)

A solution of thiophene-2-carboxyaldehyde (**7**) (0.73 g, 6.52 mmol) in ethanol (10 ml) was added to a filtered solution of 1,2-diaminobenzene (**5**) (0.64 g, 5.92 mmol) in the same solvent (50 ml). The mixture was stirred at room temperature for 24 h and then concentrated under vacuum. Upon addition of CH_2Cl_2 (50 ml), a pale brown precipitate was formed, which was filtered washed with CH_2Cl_2 (4 × 20 ml), and dried in vacuum. Yield: 0.97 g, 81%, m.p. = 246 °C; IR (KBr, cm^{-1}: 1569 m (C=N)); EA: Found: C, 65.11%; H, 4.02%; N, 13.76%; S, 14.20%. Calculated: $C_{11}H_{10}N_2S$: C, 65.32%; H, 4.98%; N, 13.85%; S, 15.84%.

2.3. Synthesis of complexes

2.3.1. 2,6-Bis[1-(2-isopropylphenylimino)ethyl] pyridineiron(II) chloride (4b)

A filtered solution of the ligand (**3b**) (0.20 g, 0.50 mmol) in THF (30 ml) was added to $FeCl_2$ (0.055 g, 0.43 mmol) in the same solvent (20 ml). After stirring of the green solution at room temperature for 24 h, *n*-pentane (80 ml) was added. Upon cooling, a dark green precipitate was formed. The product was filtered, washed with *n*-pentane (2 × 10 ml), and dried in vacuum. Yield: 0.18 g, 79%, m.p. (dec.) = 106 °C; IR (KBr, cm^{-1}: 1619 m (C=N)); EA: Found: C, 57.28%; H, 5.67%; N, 7.13%. Calculated: $C_{27}H_{31}N_3FeCl_2.2H_2O$: C, 57.88%; H, 6.29%; N, 7.49%.

2.3.2. N′-(Quinoline-2-methylene)benzene-1,2-diamineiron(II) chloride (10)

A filtered solution of the ligand (**8**) (0.08 g, 0.32 mmol) in THF (30 ml) was added to $FeCl_2$ (0.035 g, 0.28 mmol) in the same solvent (30 ml). After stirring of the light red solution at room temperature for 24 h, *n*-pentane (50 ml) was added. Upon cooling, a red precipitate was formed which was filtered, washed with *n*-pentane (3 × 20 ml), and dried. The product was crystallized from methanol. Yield: 0.08 g, 78%, m.p. = 160 °C; IR (KBr, cm^{-1}: 1622 m (C=N)); EA: Found: C, 51.24%; H, 4.03%; N, 11.13%. Calculated: $C_{16}H_{13}N_3FeCl_2$: C, 51.38%; H, 3.50%; N, 11.23%.

2.3.3. N′-(Thiophene-2-methylene)benzene-1,2-diamineiron(II) chloride (11)

A filtered solution of the ligand (**9**) (0.13 g, 0.64 mmol) in THF (20 ml) was added to $FeCl_2$ (0.068 g, 0.54 mmol) in the same solvent (20 ml). Upon addition, a dark brown solution was formed. The solution was stirred at room temperature for 24 h and then concentrated to 15 ml. Upon cooling a light brown precipitate was formed. The product was filtered, washed with THF (2 × 10 ml), diethyl ether (2 × 10 ml) and dried in vacuum. Yield 0.085 g, 48%; m.p. (dec) = 192 °C; IR (KBr, cm^{-1}: 1583 m (C=N)); EA: Found: C, 39.58%; H, 3.47%; N, 7.01%. Calculated: $C_{11}H_{10}N_2SFeCl_2$: C, 40.15%; H, 3.06%; N, 8.51%.

2.4. Polymerization experiments

All *tert*-butylacrylate, methyl methacrylate and *n*-vinylcarabazole polymerization experiments were performed under dry nitrogen atmosphere with standard Schlenk techniques. In a typical polymerization experiment, MAO was added to a suspension of the complex (2 μmol) in toluene (40 ml). After a short initiation time, the monomer was injected into the solution then the mixture was stirred at room temperature for the desired time (Table 1). The polymerization reaction was terminated by addition of acidic MeOH (60 ml). The polymer was collected, rinsed with water to remove traces of acid and dried in an oven at 60 °C until a constant weight was obtained.

Poly(*t*-butylacrylate): IR: 1727 cm^{-1} (ν CO).

Poly(methyl methacrylate): T_g (°C), 127; IR: 1730 cm^{-1} (ν CO); ^{13}C-NMR ($CDCl_3$), 176.7, 177.5, 177.8 ppm (CO).

Table 1
Polymerization results of *t*-butylacrylate[a]

Entry no.	Complex	Code	Activity[b] × 10^3	M_w[c] × 10^3	M_w/M_n[c]	T_g (°C)[d]
1	Fe(BPhEP)Cl_2	**4a**	9.2	106.0	2.3	62
2	Fe(BiPEP)Cl_2	**4b**	27.3	117.0	2.5	61
3	Fe(BBzEP)Cl_2	**4c**	34.9	172.0	2.0	62
4	Fe(BMyEP)Cl_2	**4d**	54.9	201.3	2.1	50
5	Fe(QMB)Cl_2	**10**	19.5	_[n.d.]	_[n.d.]	47
6	Fe(TMB)Cl_2	**11**	12.3	_[n.d.]	_[n.d.]	57

[n.d.] Not determined.

[a] Polymerization conditions: monomer, *t*-BA; Cat., 2.0 μmol; monomer concentration, 1.1 mol/l; MAO:M ratio, 2300:1; polymerization temperature, room temperature; solvent, toluene (40 ml); polymerization time, 24 h.

[b] Activity, g polym./mol. Cat. h.

[c] Determined by GPC relative to polystyrene standards.

[d] Determined by DSC.

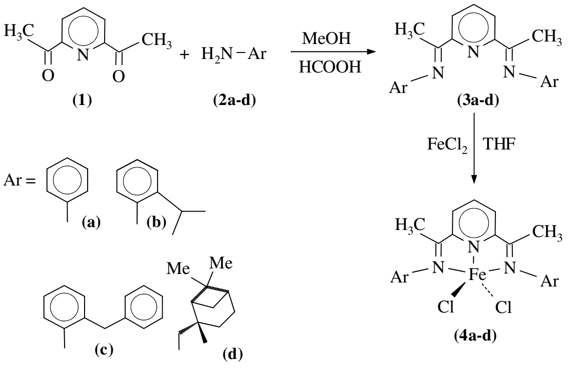
Poly(*n*-vinylcarbazole): T_g (°C), 225; IR: 1623 cm^{-1}, 1596 cm^{-1} and 742 cm^{-1} (v arom.). EA: Found: C, 86.51%; H, 5.53%; N, 6.92%. Calculated: $C_{14}H_{11}N$: C, 87.02%; H, 5.74%; N, 7.25%.

3. Results and discussion

3.1. Ligands and complexes

The tridentate 2,6-bis(imino)pyridine ligands (**3a**–**3d**) were prepared in moderate yields by the condensation reaction of 2,6-diacetylpyridine (**1**) with two equivalent of the desired amine (**2a**–**d**) in the presence of a catalytic amount of formic acid (Scheme 1). The reaction of 1,2-diaminobenzene (**5**) with one equivalent mole ratio of the aldehydes quinoline-2-carboxyaldehyde (**6**) or thiophene-2-carboxyaldehyde (**7**) afforded the aldimine ligands (**8**) and (**9**), respectively, in a good yield.

Treatment of $FeCl_2$ with the ligands (**3a**, **3b**, **3c**, **3d, 8, 9**) in THF for 24 h gave the complexes (**4a**, **4b**, **4c**, **4d**, **10**, **11**) (Schemes 1 and 2) with high to moderate yields. The isolated complexes are microcrystalline or powder-like and stable at atmospheric conditions.



Scheme 1. Synthesis and structures of the 2,6-bis(imino)pyridine ligands and their corresponding iron(II) complexes (**4a**–**d**).

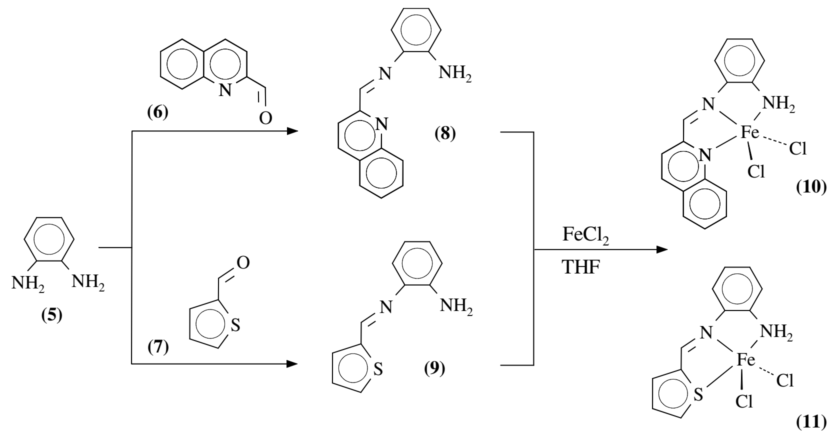
3.2. Polymerization results

The complexes (**4a**–**d**, **10**, and **11**) (Schemes 1 and 2) are activated *in situ* by the addition of MAO as an activator to a toluene solution of a chosen complex. The polymerization results are summarized in Tables 1 and 2. After stirring for about 5 min the desired amount of the monomer was added. The polymerizations were stopped by addition of MeOH/HCl solution. In general, all studied complexes possess moderate to high activities and they produce high molar mass polymers. MAO or complexes alone were not able to commence the polymerization reaction under applied polymerization conditions.

3.2.1. Polymerization of t-BA

Polymerization results of *tert*-butylacrylate (Fig. 1A) showed that the activity of the iron complexes increases with increasing the bulkiness of the substituents on the terminal groups of the ligand. This behaviour has also been observed in the polymerization of ethylene using 2,6-bis(imino)pyridine-based catalysts [12]. Complex **4d** [Fe(BMyEP)Cl_2], where the ligand carries the bulky aliphatic myrtanyl substituents on each phenyl group of the ligand, exhibits the highest activity (54.9 × 10^3 g polymer/mol catalyst. h) and produces the highest molar mass polymer (201.3 × 10^3 g/mol).

The obtained polymers were analyzed by GPC, NMR, DSC, and IR techniques. The molecular



Scheme 2. Synthesis and structures of the quinaldine- and thiophene-based ligands and their corresponding iron(II) complexes (**10** and **11**).

Table 2
Polymerization results of methyl methacrylate utilizing Fe(BMyEP)Cl_2, (**4d**)[a]

Entry no.	MAO (mmol)	Monomer (mmol)	Time (h)	Activity[b] × 10^3	$M_w \times 10^{3c}$	M_w/M_n[c]
1	7.0	149.0	12	1.40	115	2.05
2	7.0	297.0	12	11.6	154	2.09
3	18.0	297.0	12	83.4	1620	1.51
4	18.0	297.0	4	78.5	1750	1.55

[a] Polymerization conditions: Cat., 2.0 μmol; Polymerization temperature, room temperature; solvent, toluene (40 ml).
[b] Activity, g polym./mol. Cat. h.
[c] Determined by GPC relative to polystyrene standards.

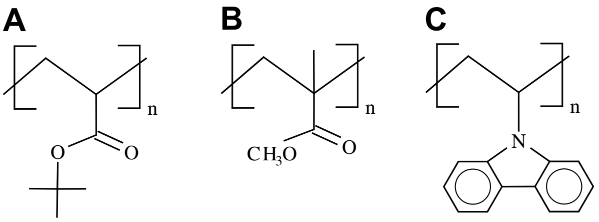


Fig. 1. Structures of the polymers poly(*t*-butylacrylate, **A**), poly(methyl methacrylate, **B**) and poly(*n*-vinylcarbazole, **C**).

weights vary with modification of the substituents on the ligand. An increase in the molecular weight of poly(*t*-BA) was also observed with increasing the bulkiness of the substituents on the phenyl ring (Table 1, entries, 1–3). Characteristically, GPC chromatograms illustrated relatively narrow molecular mass distributions (MMD) which were in the range between 2.0 and 2.5.

Various stereospecific polymerizations using Ziegler–Natta [25], metallocene [26], anionic [27,28] or radical polymerization [17] have been reported earlier. Highly isotactic poly(*t*-BA) has been synthesized using a chiral zirconocene ([m] diad 83%) [26] or with *n*-BuLi in the presence of LiOH ([m] diad 85%) [29]. The highest syndiotactic diad value reported is [r] = 63% for poly(*t*-BA) prepared by radical polymerization at low temperature [30] and a triad syndiotacticity [rr] of about 40% has been reported for anionic polymerization with diphenylmethyllithium as an initiator [31]. According to NMR spectroscopy, poly(*t*-BA) materials prepared in the present study using the complexes **4a–d**, **10**, and **11** are syndio-rich atactic with the highest [rr] diads being 37%. Similar results were previously reported by us using other types of MAO activated iron dichloride complexes, syndio-rich atactic poly(*t*-BA) with [r] around 40% were isolated at room temperature [20].

Aldimine-based complexes (**10**, **11**) showed, after activation with MAO, a relatively moderate activity towards the polymerization reaction of *t*-BA, although the sterical protection is absent in the ligand frame work. The activity of the complexes is higher than that for the complex (**4a**) with substituents free ligand and less than that for the complexes containing ligands with substituted phenyl groups. Such an increase in the activity compared to the iron(II) complex (**4a**) could be due to the formation of N–Al adduct between the free amine terminal and MAO [32].

Glass transition temperatures (T_g) of the poly (*t*-BA)s polymers ranged from 47 to 62 °C. No obvious trend between the glass transition temperature and tacticity of the polymers could be detected. Generally, these values are higher than those for the polymers obtained using a chiral metallocenes [26], organoaluminum compounds [17] or octahedral iron(II)-based complexes [20].

3.2.2. Polymerization of MMA and NVC

Complex **4d** was activated by MAO and tested for polymerization of the vinylic monomers, methyl methacrylate and *n*-vinylcarbazole.

Polymerization of methyl methacrylate with **4d**/MAO (Table 2, Fig. 1B), gave significantly high molar mass PMMA (1620×10^3 g/mol). The ^{13}C-NMR spectrum of a typical PMMA polymer is displayed in Fig. 2. Syndiotacticity of the poly (MMA) was determined with reference to the reported triad and pentad assignments [33]. Due to the α-methyl group in MMA higher syndiotacticity values were reached than with *t*-BA [34]. Signals of ^{13}C-NMR at δ 177.8, 177.5, and 176.7 ppm are assigned to mrrr, rrrr, and rmrr, respectively (Fig. 2). The ratio of these signals, 23:52:25, corresponds to a syndio-rich atactic polymer [35]. Similar results have been reported with metallocene catalysts [36]. No genuine influence from the chiral terminal moiety (myrtanyl) in the complexes (**4d**) was observed. The observed stereocontrol is most probably rising from the chain end control.

Glass transition temperature (T_g) of the isolated polymers measured by DSC was about 127 °C which is similar to PMMA that was obtained utilizing the complex, $Cp_2Zr(CH_3)_2$ [35]. Polymerizations with the complex **4d** indicate that both the monomer concentration and MAO/Cat. ratio have a direct influence on the catalyst activity, as the activity increased with the monomer concentration and the cocatalyst amount (Table 2). The molar mass is also dependent on the monomer concentration as illustrated in Table 2 (entries 1 and 2). The highest M_w, up to 1750×10^3 g/mol was obtained at $[MMA] = 7.4\ mol\ l^{-1}$ (Table 2, entry 4).

n-Vinylcarbazole (NVC) is technically an important monomer because it is one of the most sensitive photoconductive organic polymers [37]. It is quite

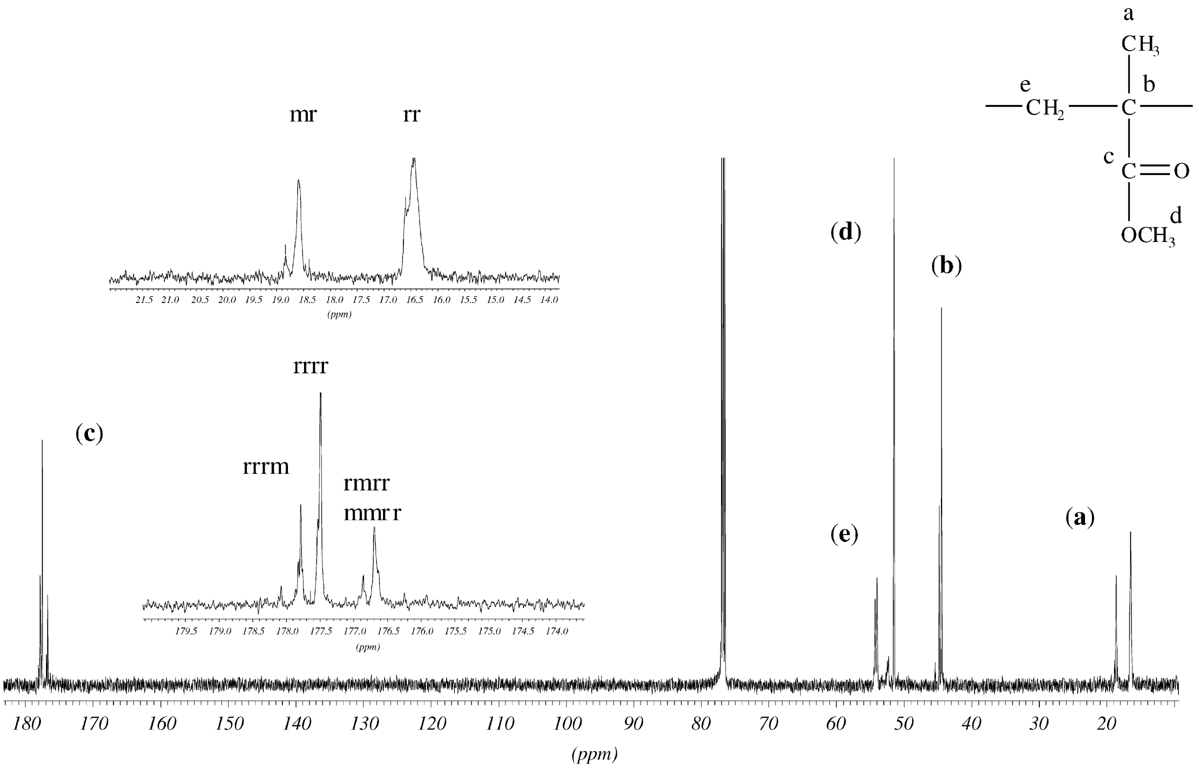


Fig. 2. ^{13}C-NMR spectrum of PMMA obtained by the catalyst system **4d**/MAO.

easy to polymerize by ionic and radical methods [38] or atom transfer radical polymerization [39].

The polymerization reaction of NVC was carried out following the same conditions applied for *t*-BA. Utilizing the catalyst **4d**/MAO, the monomer was converted to a white polymer with a high molar mass (128×10^3 g/mol) and a narrow polydispersity (1.8). According to DSC, IR and elemental analysis the material was identified as poly(*n*-vinylcarbazole) (Fig. 1c). Based on the obtained results, the catalyst system showed a moderate activity towards the polymerization of *n*-vinylcarbazole (22.2×10^3 g polym./mol. Cat. h).

4. Conclusion

In summary, a series of Fe(II)-based transition metal complexes bearing 2,6-bis(imino)pyridyl, quinolinaldimie, and thiophenaldimine ligands have been investigated for the polymerization of *tert*-butylacrylate after activation with MAO. Polymerization results showed that bis(imino)pyridyl-based complexes are more active than the complexes containing the aldimine ligands. In addition, the ketimine complexes having bulky aliphatic substituents have highest activities in *t*-BA polymerizations while activity of the complexes with aromatic substitutes, is in general lower and dependent on the substituents on the aniline. The potential of iron(II) complexes in homopolymerization of various polar monomers has been demonstrated as polymerization experiments indicated that these complexes are also active towards the polymerization of methyl methacrylate, and *n*-vinyl carbazole.

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