

Copolymerization of Methyl Methacrylate with 4-Vinylpyridine Initiated by a Novel Ni(II) α -Benzoinoxime Complex

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Received 4 June 2007; accepted 6 October 2007

DOI 10.1002/app.27476

Published online 10 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Copolymerizations of methyl methacrylate (MMA) with 4-vinylpyridine (4VP) were performed from different monomer feed ratios in 1,4-dioxan at 30°C under free radical initiation experimental conditions, using Ni(II) α -Benzoinoxime complex as initiator. The obtained copolymers (PMMA4VP) were examined by FTIR and ¹H NMR spectroscopies. The composition of these copolymers was calculated, using ¹H NMR spectra and elemental analysis. Monomer reactivity ratios were estimated from Fineman–Ross (FR, $r_m = 0.550$, $r_v = 1.165$) and Kelen–Tudos (KT, $r_m = 0.559$, $r_v = 1.286$) linearization methods, as well as nonlinear error in variables model (EVM) method using the RREVM computer program (RREVM, $r_m = 0.559$, $r_v = 1.264$). These values suggest that MMA-4VP pair copolymerizes randomly. ¹H NMR spectra provide information about the stereochemistry of the copolymers in terms of

sequence distributions and configurations. These results showed that the age of the Ni complex has an impact not only on its activity towards polymerization reactions but also on the features of the corresponding copolymers, whereas the chemical composition was insensitive to this prominent factor. The mechanism of MMA-4VP copolymerization is consistent with a radical process as supported by microstructure and molecular weight distribution studies. Thermal behaviours of these copolymers were investigated by differential scanning calorimetry and thermogravimetric analysis. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3963–3973, 2008

Key words: methyl methacrylate; 4-vinylpyridine; copolymerization; Nickel complex; monomer reactivity ratios; thermal properties; degradation

INTRODUCTION

There has been a great interest over the last few years in the use of late transition metal catalysts for the homo- and co-polymerization of olefins.^{1–4} Among them, Nickel complexes have been extensively studied. Ni(II) α -diimine catalysts, when activated with methylaluminumoxane (MAO), exhibit high activity towards the polymerization of ethylene, 1-hexene, and propylene as well as their block copolymerization.^{5–7} Moreover, this kind of catalysts can be used as ATRP catalysts for the polymerization of styrene and methyl methacrylate (MMA) with poor to moderate control process.⁸ Divalent nickel complex bearing acetylide ligand Ni(C \equiv CPh)₂(PBU₃)₂ has been a potential effective catalyst for the ATRP of MMA.⁹ Several Ni(II) and Ni(0) complexes with selected ligands induced efficient living radical polymerization of MMA and alkyl acrylates

with a moderate activity.¹⁰ Also, NiBr₂(PPh₃)₂ mediated controlled radical copolymerization of MMA and functionalized methacrylate monomers such as 2-hydroxyethyl methacrylate (HEMA) is reported.¹¹ However, a variety of nickel catalysts involving N- or O- donated ligand in combination with modified MAO were highly active for the homopolymerization of norbornene at 25°C while its copolymerization with MMA was unsuccessful.¹²

In this contribution, our attention focuses on a new neutral Nickel(II) complex bearing α -Benzoinoxime chelating ligand that formation process¹³ is described in Scheme 1.

Hank et al.¹³ have reported that the metal center Ni(II) of a recently synthesized Ni(II) α -Benzoinoxime complex undergoes sluggishly oxidation, in its solid state, by the ligand to higher oxidation state Ni(IV). This oxidation give rise to a progressive structure change of the complex from square-planar Ni(II)-complex to octahedral Ni(IV)-complex, Scheme 1.

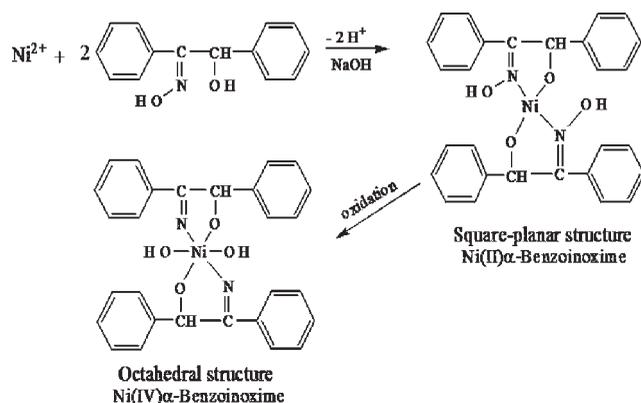
In a previous study,¹⁴ we have established that this complex can act as a single-component initiator for the MMA polymerization over the temperature range 25–60°C.

As an extension of our study in this area, we report herein the synthesis and characterizations of

This work is dedicated to the memory of the regretted professor F. Amrani.

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Journal of Applied Polymer Science, Vol. 107, 3963–3973 (2008)
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Scheme 1 Formation and suggested structure of Nickel (II) α -Benzoinoxime complex.

different copolymers of MMA with 4-vinylpyridine (4VP) in 1,4-dioxan, at room temperature, using Ni(II) α -Benzoinoxime complex as initiator. The choice of 4VP is related to the great interest of corresponding copolymers. These copolymers can interact with other polymeric materials through specific interactions to form miscible polymer blends with improved properties.^{15,16}

Besides, the chemical composition of the copolymers and comonomer sequence depends on the relative reactivity between the comonomers. Hence, the reactivity of MMA and 4VP in the copolymerization process were quantified by the estimation of the corresponding monomer reactivity ratios (MRRs), r_m and r_v , according to the general copolymerization equation by application of the well known linearization methods Fineman–Ross (FR)¹⁷ and Kelen–Tudos (KT),¹⁸ whose are appropriate at low-conversions. We must pointed out that the MRRs, obtained from these methods, are only approximate and are frequently employed as good starting values for the estimation of more reliable values using a computational procedure. This method is based on a statistically valid nonlinear minimization algorithm, Reactivity Ratios Error in Variable Method (RREVM),¹⁹ which allow one to take properly into account all the sources of experimental error. For this reason, the RREVM program has also been applied to recalculate the MRRs values.

Some features of the copolymers and the striking influence of the complex age on its activity are also discussed through this study.

EXPERIMENTAL

Materials

MMA and 4VP from Aldrich were purified by distillation under reduced pressure. Ni(II) α -Benzoinoxime was synthesized according to a procedure

reported in the literature.¹³ All solvents (Dioxan, Chloroform) and precipitants (Methanol, Petroleum ether) from Aldrich (analytical grade) were used without purification.

Copolymerization

Copolymerizations of MMA with 4VP, using various monomer feed ratios, were carried out in 1,4-dioxan at 30°C with Nickel(II) α -Benzoinoxime complex as initiator at constant total weight of monomers under the nitrogen atmosphere. Reaction conditions are given in Table I. Pre-determined quantities of comonomers were introduced into a three-necked round bottom flask (equipped with magnetically stirrer, reflux condenser and dropping funnel) and the mixture was flushed with oxygen-free nitrogen for 20 min. Then the solution was kept in a thermostated water bath at 30°C \pm 1°C. At the same time, the complex solution (1% w/w based on total MMA and 4VP monomers) was placed in the dropping funnel under nitrogen flux. The copolymerization reaction was triggered by quick addition of the complex solution into the mixture flask. After a given time, the reaction was stopped by exposing to air. The copolymers samples were precipitated into a large excess of petroleum ether (methanol for MMA homopolymer), filtered and dried in a vacuum oven at 50°C until constant weight. The purification of the copolymers was achieved by dissolution/precipitation procedure in the chloroform/petroleum ether system. The conversions were determined gravimetrically.

Some trial experiments of MMA polymerization mediated with Ni(II) α -Benzoinoxime complexes (of different ages) were carried out in a similar manner.

Measurements

FTIR spectra of the synthesized PMMA and copolymers were recorded on a Nicolet 560 spectrometer in 4000–400 cm^{-1} range, where 62 scans were taken at 2 cm^{-1} resolution. Samples as thin films cast on KBr disks were prepared from chloroform polymer solution (3% w/v). After a slow evaporation of the solvent, they were dried in a vacuum oven at 65°C for several days.

The ¹H NMR spectra of all the polymers samples were run on a Bruker 500 MHz spectrometer at room temperature, using CDCl₃ as solvent and tetramethylsilane as internal standard.

The molecular weights (M_n and M_w) and polydispersity index (M_w/M_n) of PMMA and PMMA4VP copolymers were measured on a waters 590 gel permeation chromatograph, equipped with styragel HT columns (10³–10⁶ g/mol), at 25°C using THF as

TABLE I
Copolymerization of MMA with 4VP Using Ni(II) α -Benzoinoxime Complex at 30°C from Various Initial Monomer Mixtures^a

Entry	Complex ^b	Age (months)	4VP feed		Time (h)	Yield (%)	4VP Composition in copolymers (mol %)		[η] (dL/g)	$M_w \times 10^{-4}$ (g/mol)	$M_n \times 10^{-4}$ (g/mol)	M_w/M_n
			fraction (mol %)	(mol %)			(mol %)	(mol %)				
1 ^c	C-3	16.5	0.00	0.00	4	3.896	0.00	0.00	—	—	—	—
2	C-3	16.5	0.00	0.00	4	13.722	0.00	0.00	1.360	63.364	24.170	2.62
3	C-2	26.0	0.00	0.00	24	12.500	0.00	0.00	0.578	16.804	6.733	2.5
4	C-1	40.8	3.82	1.184	24	1.184	5.12	5.12	0.452	7.628	2.366	3.22
5	C-1	41.2	4.77	1.006	24	1.006	8.08	8.08	0.330	5.463	2.442	2.24
6	C-3	17.0	4.77	5.042	4	5.042	7.90	7.90	0.587	8.281	3.497	2.37
7	C-3	17.0	6.69	3.787	4	3.787	11.48	11.48	0.497	5.253	1.755	2.99
8	C-3	16.8	7.65	4.134	4	4.134	12.08	12.08	0.602	6.768	1.761	3.84
9	C-1	41.1	9.57	0.985	24	0.985	17.69	17.69	0.278	—	—	—
10	C-2	27.4	24.10	5.745	24	5.745	32.34	32.34	0.308	—	—	—
11	C-1	37.5	48.78	3.450	24	3.450	59.90	59.90	0.245	—	—	—

^a Experimental conditions: Monomers/Solvent: 1/1 (weight ratio); comonomers/Ni complex: 10³ (weight ratio); Solvent: Dioxan; Total solution volume: 400 mL.

^b C-1, 2, and 3 complexes are synthesized repeatedly according to the same procedure.

^c Polymerization of MMA in chloroform as solvent.

eluent. The system had previously been calibrated with standard polystyrenes (PS).

Viscosity measurements were carried out in dioxan at 30 \pm 0.1°C using a Schott Geräte automatic dilution viscosimeter. Intrinsic viscosities [η] of these polymers, determined from the well known Huggins equation,²⁰ are listed in Table I.

DSC thermograms were recorded on a PerkinElmer Pyris I calorimeter, under dry nitrogen (50 cm³ min⁻¹). For all measurements, the samples weighting about 10 mg were hold for 3 min at 0°C then heated until 200°C with a rate of 20°C min⁻¹. After keeping at this temperature for 3 min, the samples were cooled from 200 to 40°C at 80°C min⁻¹ then followed by a similar second scan. The glass transition temperatures T_g were determined during the second heating run at the midpoint of the transition.

Thermogravimetric analysis (TGA) was performed on a Q500 thermal analyzer under nitrogen atmosphere, in the temperature range 40–495°C with a heating rate of 10°C min⁻¹. The average sample weight was 10 mg and the nitrogen flow-rate was 50 cm³ min⁻¹.

RESULTS AND DISCUSSION

Features of homo- and co-polymerization

The novel neutral Nickel(II) α -Benzoinoxime complex (NBO) is air and moisture-stable and soluble in common organic solvents. Since NBO triggers MMA polymerization with moderate activity via a radical mechanism,¹⁴ the copolymerization of MMA with 4VP in various monomers feeds was herein investigated at 30°C. To this end, we have selected three complexes (C-1, C-2, and C-3) obtained from repeated syntheses according to a same procedure.¹³

The choice of the polymerization solvent is a very important factor since the complex activity is sensitive to its polarity. Thus, complex C-3 (16.5 months old) was tested in MMA polymerization at 30°C for 4 h in chloroform ($\epsilon = 4.7$) and in dioxan ($\epsilon = 2.2$), which are considered, respectively, as suitable and bad solvents for 4VP homopolymerization. In agreement with our previous study¹⁴ that showed that the monomer conversion depressed with increasing solvent polarities, the dioxan led to higher yield (13.72%) than chloroform (3.89%), Table I. On the basis of this result, these experiments were conducted exclusively in dioxan.

We have, in a first step, undertaken the copolymerizations for 24 h using C-1 and C-2 (different ages) as initiators. The obtained results are collected in Table I. As it can be seen, NBO complex was an effective initiator in the copolymerization reaction under mild conditions to give soluble copolymers.

TABLE II
Black Experiments of Homopolymerization^a of MMA
Initiated by Ni(II) α -Benzoinoxime Complex as Function
of its Age

Complex ^b	Age (months)	T (°C)	Time (h)	Yield (%)
C-1	1	25	5	Traces
	6	25	5	4.8
	36.5	30	24	15
	42	30	5	0
C-2	0.5	30	3	2.5
	26	30	24	12.5
C-3	1	30	5	Traces
	3.5	30	5	4.5
	16.5	30	4	13.72
	19	30	7	8
	19.5	30	7	0

^a Polymerization conditions: MMA/Solvent: 1/1 (volume ratio); Total volume: 10 mL; Ni complex/MMA: 1/10³ (weight ratio).

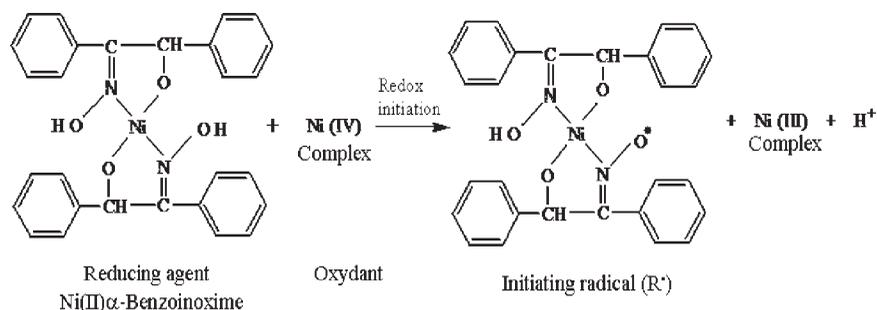
^b C-1, 2, and 3 complexes are synthesized repeatedly according to the same procedure.

However, it exhibited only a low activity since conversion did not exceed 5.8%. These results revealed that the conversion depends simultaneously on two effects, namely the 4VP incorporation in copolymer chains and the age of the complex used.

To provide more convincing evidence for the occurrence of these effects, two series of experiments were carried out. In the first one, the progression of complex activity as function of its age was monitored by black experiments of MMA polymerization using three complexes (C-1, C-2, and C-3), as shown in Table II. It seems clear that the complex age has a prominent impact on polymerization reaction. As it evolves, each complex exhibits a gradual rise of its activity until an optimum beyond which a drop in activity is expected and followed by a complete inactivity towards MMA polymerization. In fact, as we have previously discussed in the MMA polymerization study,¹⁴ the striking influence of the complex age on its activity was closely linked to the sluggish oxidative effect of the α -Benzoinoxime ligand, which convert progressively the Ni(II) complex into Ni(IV)

complex giving rise to a mixture of the two complexes. The comparison between the behavior of freshly synthesized complex (5 days old) and older one (3 years old) in several MMA polymerization, run under the same tested conditions, revealed that both complexes were inactive within 6 h. This result has allowed us to conclude that in the former case, the Ni(IV) complex was not yet formed from Ni(II) complex and therefore this later cannot mediate the polymerization alone. In the second case, the Ni(II)-complex disappears entirely by the oxidation effect into Ni(IV) complex that alone, proved to be unable to promote the polymerization reaction. Besides, an improvement in activity of the complex was obvious when its age advanced accompanied by a decrease beyond an optimum. Additionally, the MMA polymerization reaction was halted in presence of radical scavenger, TEMPO, indicating a radical pathway. Thus, according to other experiments results undertaken in our previous study,¹⁴ we have concluded that both Nickel chelates are involved in redox initiation mechanism, a very effective process for generating free radicals, under milder conditions by single-electron transfer process. Indeed, in agreement with Sarac investigations,²¹ we have suggested that Ni(II) complex acts as reducing agent that subsequently generate radicals initiating species, while Ni(IV) chelate acts as strong oxidant agent that promote an homolytic cleavage of the O—H bond in Ni(II) chelate. This breakdown is accompanied by direct electron transfer from the reducing agent to Ni(IV) species, as depicted in Scheme 2. Thereby, the evolution of the activity of our Ni complex as a function of its age is governed by the variation of the relative ratios Ni(II)/Ni(IV) species in the complex mixture at the solid state.

Otherwise, Sawamoto et al. pointed out that the use of additives like aluminum alkoxides improves the yields of styrene²² and alkyl methacrylates^{23,24} homo- and co-polymerizations. Also, Masuda et al.²⁵ reported that polymerization of phenylacetylene with [(nbd)RhCl]₂ catalyst proceeded instantaneously by addition of cocatalysts such as Et₃N, while



Scheme 2 The proposed redox initiation mechanism between Nickel(II) α -Benzoinoxime and Nickel(IV) α -Benzoinoxime complexes pairs.

TABLE III
Effect of Additive on MMA Polymerization by Ni(II) α -Benzoinoxime Complex
(C-4, 2.5 months old)^a

Entry	Et ₃ N/Ni (mol ratio)	Yield (%)	Activity (10 ⁻³) (g _{poly} /mol _{Ni} h)
1	0	2.66	2.717
2	100	4.30	4.392
3	200	6.04	6.169
4	400	16.24	16.588
5	500	14.18	14.483
6	800	15.90	16.240
7	1000	13.76	14.054
8	2000	9.52	9.724

^a Polymerization conditions: MMA/Solvent: 1/1 (volume ratio); Total volume: 10 mL; Ni complex/MMA: 1/10³ (weight ratio); Temperature: 30°C; Time: 5 h.

a sluggish reaction is observed in the absence of this cocatalyst. On this basis, a series of MMA polymerization were achieved at 30°C in dioxan, using NBO (C-4, 2.5 months old) with Et₃N by varying the mole ratio of Et₃N/Ni complex and keeping the concentration of monomer and initiator constant, Table III. As expected, a low conversion (only 2.6%) is obtained in absence of Et₃N, while an optimum value of 16% is reached when Et₃N/Ni molar ratio is 400. Also, the activity was significantly improved from 0.27.10⁴ to 1.6.10⁴ g_{poly}/mol_{Ni}.h but remained moderate.

Further kinetic investigations are now in progress in order to evaluate the concentration of Ni(II) species corresponding to the optimal activity using a titrimetric procedure.²⁶

In the second series, similar MMA-4VP copolymerization based on C-3 complex (16.5–17 months old) were carried out (Table I). It is clear that this complex exhibits a greater activity than the others. For instance, from equal 4VP feed fraction the C-1 complex (41 months old) led to 1% conversion after 24 h while 4 h only were enough for C-3 complex to reach 5% in conversion.

On the other hand, an increase of 4VP amount in the feed slowed down gradually the reaction rate. A drop in copolymer yields is also observed as compared with that of MMA polymerization suggesting that 4VP slow down the chains growth in copolymerization reaction.

We have also tried to polymerize 4VP in dioxan under the same conditions, somewhat surprisingly Nickel (II) α -Benzoinoxime was completely inactive. A similar result was observed with Ni(acac)₂/triethylaluminum (TEA) catalyst system and only low activity was derived from Ni(acac)₂/methylaluminumoxan (MAO).²⁷ Indeed, the 4VP homopolymerization is very a challenging problem for atom transfer radical polymerization²⁸ and controlled radical polymerization,¹⁰ since the 4VP can coordinate to the metal complex inducing subsequent decrease in its activity. Moreover, it is well-known that Nickel compounds are capable to form stable complexes with ligands

bearing nitrogen atom,²⁷ as a result we believe that 4VP monomer can also competitively act as ligand by coordination to Nickel center of our complex giving rise to reduce in its activity towards copolymerization.

It is worthwhile to mention that the low copolymer yields obtained at 30°C are also related to decrease in complex activity resulting from decrease of polymerization temperature, as evidenced previously in MMA polymerization.¹⁴ Similar results were reported for Nickel- or Palladium-based in homo- and co-polymerization of several monomers such as styrene,²⁹ norbornene and its derivatives³⁰ as well as substituted acetylenes.³¹ Accordingly, Liaw et al.³² showed that in presence of (Pd(CH₃CN)₄)(BF₄)₂ complex, the yields of carbonmonoxide–phenylacetylene copolymers reached 79% within 2h at 90°C, while a drop about 2% is observed at 40°C.

Characterization of copolymers

FTIR spectroscopy

The FTIR spectra of copolymers as compared with that of PMMA exhibit several characteristics bands of 4VP units (Fig. 1). Indeed, the two bands at 3068 and 3020 cm⁻¹ are due to C–H stretching vibration resulting from the pyridine ring and the other bands located at 1597, 1558, and 1414 cm⁻¹ are assigned to C=N stretching vibration of pyridine ring.

The intensity of all the above absorptions increased with an increase of 4VP content in monomer feed confirming its incorporation into the copolymer chains. Moreover, the absence of absorption near 1625 cm⁻¹ in the copolymers due to alkenes bond is indicative of the participation of vinyl group of 4VP monomer in the copolymerization.

¹H NMR spectroscopy

Copolymer composition

¹H NMR spectra of several copolymers and PMMA as reference, along with the assignment of various resonance signals are shown in Figure 2.

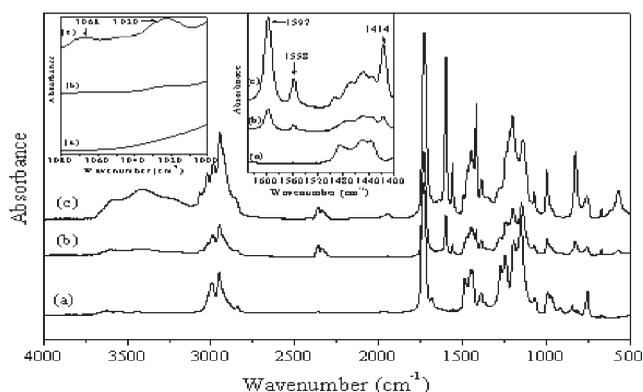


Figure 1 FTIR spectra between 500 and 4000 cm^{-1} for PMMA (a) and MMA-4VP copolymers; mol % of 4VP in feed is 24.1% (b); 48.78% (c).

The copolymer compositions were estimated from the relative intensities of the meta aromatic proton signals of 4VP with those of methoxy group of MMA according to the expression below:

$$F_v = 3S_v / (2S_m + 3S_v) \quad (1)$$

where: S_v and S_m are the integrated peaks area of H_v and H_m , respectively.

The copolymer compositions data are collected in Table I. As it can be seen, the molar compositions of the resulted PMMA4VP copolymers are modulated with the mole comonomer feeds regardless the crucial role of complex age in its reactivity towards copolymerization reaction. The solid curve exhibited in Figure 3, shows a high introduction of 4VP in co-

polymer chains. It is also interesting to note that the level of 4VP incorporation is quite higher in presence of our Ni complex than conventional free radical initiator.³³

Copolymer stereochemistry

The ^1H NMR copolymer signals exhibit an overall shift toward higher fields with increasing 4VP unit in the copolymer chains due to the well-known screening effect of aromatic nucleus. Similar behavior was observed by Natanshon et al. with copolymers of methyl acrylate (MA) or MMA with 2VP or 4VP.^{34–36} Simultaneously, The signals belonging to aromatic, methoxy, and $\alpha\text{-CH}_3$ groups are split with an increase in 4VP content in copolymers due to their compositional (monomer sequence distribution) as well as configurational sensitivity. In agreement with Natanshon et al. studies, these signals are tentatively assigned in terms of triads and are depicted in Figure 4, where M and V indicate MMA and 4VP, respectively.

Aromatic signal

The ortho and meta proton signals seems to be sensitive only to the triad sequence distribution and not to the configuration, also their levels shift to higher field are about 0.174 and 0.0176 ppm, respectively. Natanshon³⁶ has attributed such shifts to the increase content of VVV triads, which resonate at higher fields and to the decrease content of VVM and MVM triads that resonate at lower fields, part I

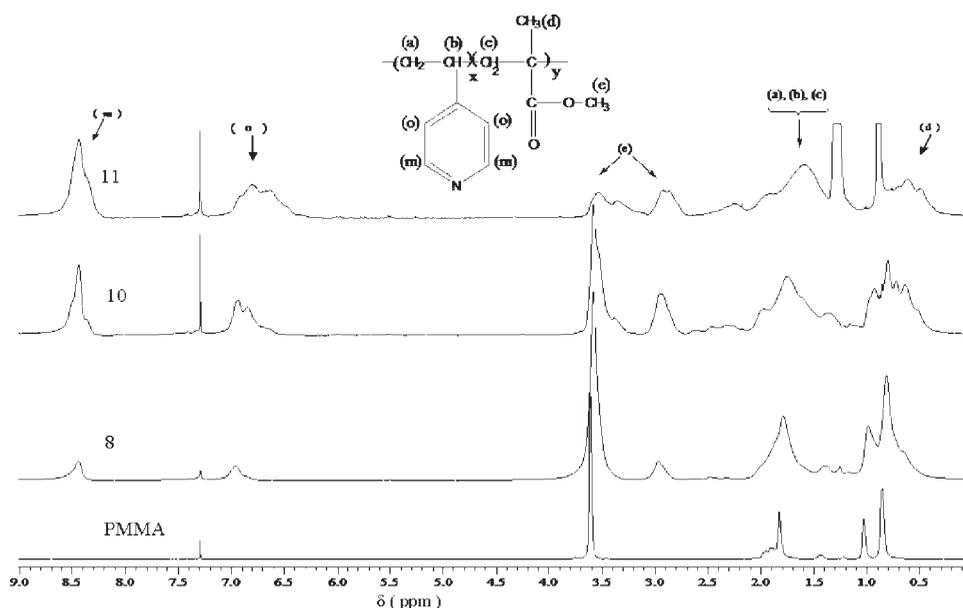


Figure 2 ^1H NMR spectra of PMMA and MMA-4VP copolymers; mol % of 4VP in feed is 7.65% (8); 24.1% (10), as in Table I.

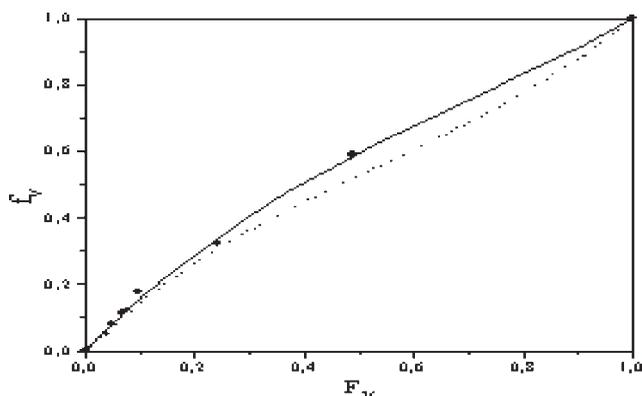


Figure 3 Copolymer composition diagram for (MMA-4VP) copolymers obtained in presence of Ni(II)complex (—●—) along with the theoretical composition curve (.....) obtained from the copolymer composition equation using terminal model reactivity ratios $r_m = 0.574$, $r_v = 0.79$.

in Figure 4. In addition, the splitting of ortho proton signals is more pronounced than meta ones, while no such splitting is reported for 4VP homopolymer. Unfortunately, this region cannot be investigated in v-centered sequence distribution calculation owing to the poor resolution of our spectra. Indeed, Natanshon and Eisenberg³⁷ have related the magnitude of the splitting to the nature of the deuterated solvent used. Thus, the spectra recorded in DMSO solvent at 70°C provide better splitting than in chloroform or benzene because it lacks interfering signals.

Methoxy signal

This group splits mainly into two signals due to the screening effect of the neighboring 4VP ring, part II in Figure 4. The intense one at about 3.57 ppm, similar to that of PMMA, belongs to M_rM_rM triads sequences. The smaller one at about 2.9 ppm can be assigned to $M_mM_mV + M_rM_mV$ triads. As the incorporation of 4VP increases, their relative intensities decrease accompanied by the appearance of two new signals at 3.52 and 3.37 ppm, being overlapped by the main peak at 3.57 ppm whose belong to M_mM_rV and M_rM_rV triads, respectively.

α -CH₃ signal

From Figure 4 in part III, this signal shows in PMMA spectrum three peaks at 0.82, 1.00, and 1.21 ppm due to the shielding induced by the carbonyl group of the MMA units, assigned to syndiotactic (rr), heterotactic (mr + rm), and isotactic (mm) of MMM triads, respectively.³⁸ In the copolymers spectra, the M_rM_rM triad signal undergo splitting to three other signals at about 0.72, 0.63, and 0.5 ppm, whose intensities increase with increasing 4VP units assigned respectively to $(M_mM_mV + M_rM_rV)$,

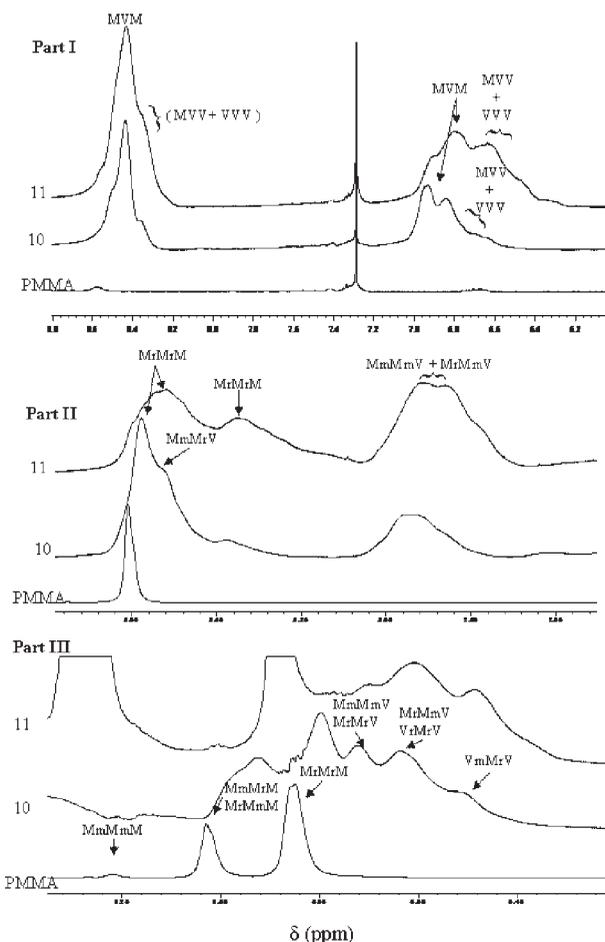
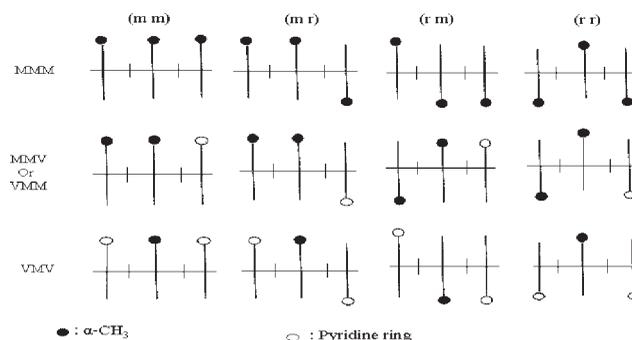


Figure 4 Expanded ¹H NMR spectra of aromatic (I), methoxy (II), and α -CH₃ (III) resonance signals together with triad distribution of PMMA and MMA-4VP copolymers; mol% of 4VP in feed is 24.1% (10); 48.78% (11), as in Table I.

$(M_rM_mV + V_rM_rV)$ and V_mM_rV triads, as proposed by Natanshon.³⁴ Scheme 3 represents the monomer sequence distribution in terms of (M) centered triads and the relative stereochemical configuration.

On the other hand, the microstructure of the PMMA obtained with Nickel(II) α -Benzoinoxime 67% rr,



Scheme 3 Schematic representation of M centered triads in MMA-4VP copolymers.

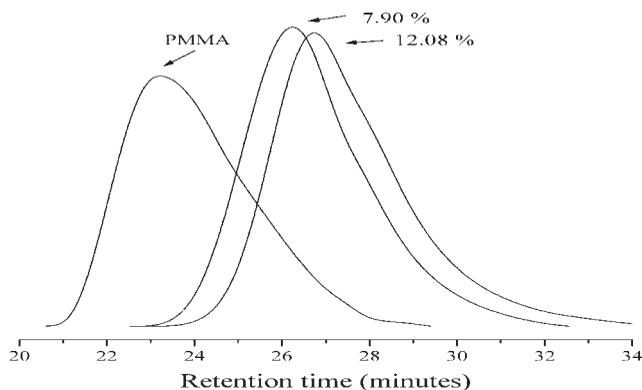


Figure 5 GPC profiles of PMMA (2) and typical MMA-4VP copolymers obtained by Ni(II) complex, monitored by RI detector, mol % of 4VP-units: 7.90% (6) and 12.08% (8), as in Table I.

30% mr, and 2% mm is close to that observed with conventional initiator.³⁸ It seems obvious that the present copolymerization also proceeds via a free radical mechanism.

Determination of molecular weights and viscosity measurements

The number and weight-average molecular weights and the polydispersity index of PMMA and some of the PMMA4VP copolymers are collected in Table I. Figure 5 exhibits a unimodal molecular weight distribution of PMMA and a typical copolymer. These results show that the molecular weights (M_w , M_n) decreased with an increase of 4VP content in the copolymers. The polydispersity values are slightly broad ($1.67 < M_w/M_n < 3$) supporting the occurrence of a conventional radical process and the termination reactions proceed mainly by disproportionation.

Also, as can be seen from Table I, the molecular weight values are sensitive to the activity of the complex that is related to its age. In other words, enhance in complex activity allows to a rise in molecular weights. For instance, among the selected complexes the most active one (C-3) provides the highest molecular weight values for PMMA (entry 2 and 3) and copolymers containing similar 4VP units (entry 5 and 6). The intrinsic viscosities values are also summarized in Table I, where a similar trend was observed.

Determination of monomer reactivity ratios

From monomer feed ratios and copolymer compositions the MRRs of MMA (r_m) and 4VP (r_v) were evaluated at low conversion (<6% in weight) by FR and

KT ($\alpha = 7.59$) according to eqs. (2) and (3), respectively.

$$G = -Er_m + r_v \quad (2)$$

$$\eta = (r_m + (r_v/\alpha))\xi - r_v/\alpha \quad (3)$$

where: $G = H(h-1)/h$ and $E = H^2/h$; With H and h are molar fraction ratios of the monomers in the feed (F_m/F_v) and copolymers (f_m/f_v), respectively.

$$\eta = G/(\alpha + E); \xi = E/(\alpha + E) \text{ and}$$

$$\alpha (\text{arbitrary constant}) = (E_{\max} \times E_{\min})^{1/2}$$

The linearity of the corresponding graphical plots in Figure 6(a,b) indicates that the reactivity of the growing polymer radical depends on the terminal model of copolymerization. The MRRs were also calculated by means of RREVM computer program, using as starting values those obtained by the KT method, which provides a higher confidence level of data with regard to FR one. These values were generated using errors of 1% for the monomer feed compositions and of 3% for the copolymer compositions. The accuracy of the estimated data is represented in Figure 7 where the 95% joint confidence interval is drawn.

The r_m and r_v values obtained by the FR and KT methods as well as the RREVM procedure are compiled in Table IV, where a good agreement between the different sets of data is observed.

Using the RREVM values as a reference, it is possible to note that the chain growth reactions proceed mostly by $\sim 4VP \cdot$ growing radicals. The $1/r_m \sim 1.7$ value indicates that $\sim MMA$ radicals slightly promote cross propagation, while $1/r_v \sim 0.7$ value points to higher tendency of the $\sim 4VP \cdot$ radicals to add 4VP monomer. The product $r_m \cdot r_v = 0.7 (<1)$ indicate that the copolymerization of MMA with 4VP leads to random distribution somewhat enriched with 4VP.

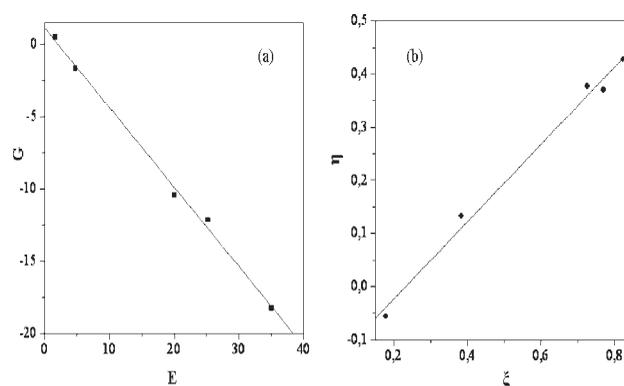


Figure 6 FR (a) and KT (b) plots for MMA-4VP copolymers obtained in presence of Ni(II) complex.

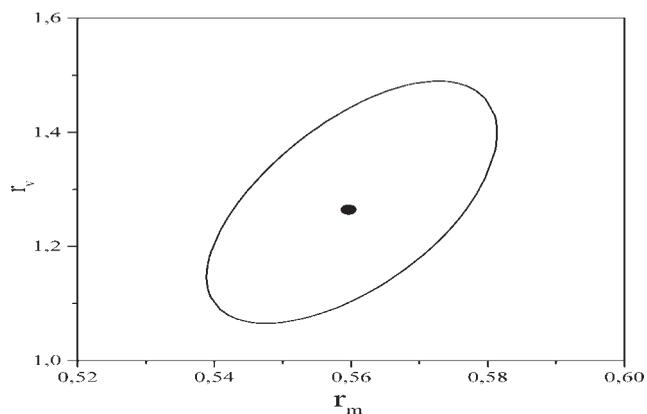


Figure 7 95% Confidence region for the evaluated values of r_m and r_v by RREVM method.

The greater insertion frequency of 4VP units in copolymer chains is tightly linked to the competitive effects of the side-chain groups on the mutual reactivity of both comonomers. Indeed, the presence of an aromatic group in 4VP originates a reactive monomer because of the high electronic withdrawal stabilization by resonance of the radicals generated during the copolymerization process. In counterparts, the presence of an electron-attracting carbonyl group in MMA monomer, brings out a positive charge density on carbon atom attached to the carbonyl that provides a considerable electron attraction in \sim MMA. radicals. It is however obvious that the resonance stabilization effect prevails and thus a preference for 4VP incorporation in chains.

Similar trend was observed in conventional copolymerization of methyl acrylate-4VP ($r_m = 0.18$, $r_v = 1.77$),³⁵ whereas a alternation tendency is reported with the *tert*-butyl acrylate-4VP pair ($r_{tBA} = 0.054$, $r_v = 0.046$).³⁹ The r_v value of 4VP obtained by Nickel complex is somewhat higher than that tabulated for conventional copolymerization of MMA-4VP ($r_m = 0.574$, $r_v = 0.79$),³³ while the r_m one is in good agreement.

Thermal behavior of the copolymers

Differential scanning calorimetry (DSC)

Figure 8 displays the DSC curves of PMMA and selected copolymers. As expected, all the recorded thermograms exhibit a single T_g throughout the whole composition range, indicating the absence of a mixture of homopolymers or the formation of a block copolymer. The T_g values are compiled in Table V. As it can be seen, these values increase generally with increasing 4VP content in the copolymer chains. However, it is well known that the increase in T_g is due to the decrease in segmental mobility of polymer chains that can be related to a rise in the

TABLE IV
Copolymerization Parameters for MMA (r_m) and 4VP (r_v) in MMA-co-4VP Copolymer

Method	r_m	r_v	$r_m \cdot r_v$
Fineman-Ross	0.550	1.165	0.64
Kelen-Tüdös	0.559	1.286	0.71
RREVM	0.559	1.264	0.70

molecular weight, i.e. chain polymer length. As expected, the T_g depression observed for PMMA4VP copolymer with 32.34% 4VP content (entry 10) can be linked to its low molecular weight (see Table I), that is strongly affected by the age complex effect as discussed below. Unlike the above result, in the case of copolymers obtained from the same 4VP feed fraction 4.77% (entry 5 and 6 in Tables I and V), a high T_g value was observed for low molecular weight (low chain length) when the copolymer is originated from C-1 (less active) than that issue from C-3 (more active). This fact can be explained by the competitive entanglement effect of the polymer chains brought about by the α -methyl groups in MMA units, which prevent the mobility of the relatively short polymer chains and then increase the T_g value.

Thermogravimetric analysis

Figure 9 shows the TGA thermograms and derivative curves DTG of PMMA and of typical PMMA-4VP copolymers. The temperature of maximum degradation, percentage weight loss in each stage of degradation and residual weight at 495°C are summarized in Table V. As it can be seen, the thermal degradation of PMMA starts at \sim 220°C and proceeds in two distinctive steps. The first one appears in the 250–300°C temperature range with a weight loss of about 9%, which is followed by the intense

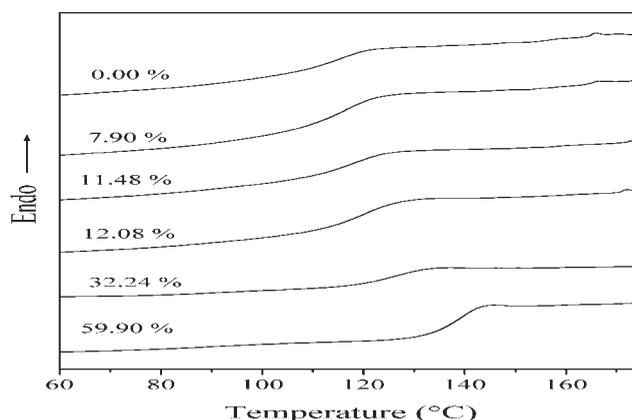


Figure 8 DSC thermograms of PMMA (3) and some MMA-4VP copolymers with different compositions (mol % of 4VP-unit as in Table I, entry 6–8 and 10–11).

TABLE V
Thermal Behaviours of Poly(MMA-co-4VP) Copolymers with Different Compositions

Entry ^a	Content of 4VP-units (mol %)	DSC analysis				TGA analysis, Weight loss (%) at		Residual weight (%)
		T_g (°C)	T_{d1} (°C)	T_{d2} (°C)	T_{dmax} (°C)	T_{d1}	T_{d2}	
2	0 ^b	117	280	369	369	9.38	70.00	0
3	0 ^c	115	288	369	369	22.18	75.14	0
4	5.12	–	284	339	339	21.32	67.73	8.24
5	8.08	123	288	340	340	20.74	66.64	9.64
6	7.90	117	306	358	358	30.18	73.98	7.54
7	11.48	118	309	349	309	33.04	67.66	9.87
8	12.08	120	310	354	310	32.12	69.26	9.42
9	17.69	132	315	–	315	40.26	–	12.86
10	32.34	126	309	–	309	41.84	–	9.6
11	59.9	139	317	–	317	46.79	–	7.61

^a As in Table I.

^b MMA Polymerization time of 4 h with Ni(II)complex (C-3, 16.5 months old).

^c MMA Polymerization time of 24 h with Ni(II)complex (C-2, 26 months old).

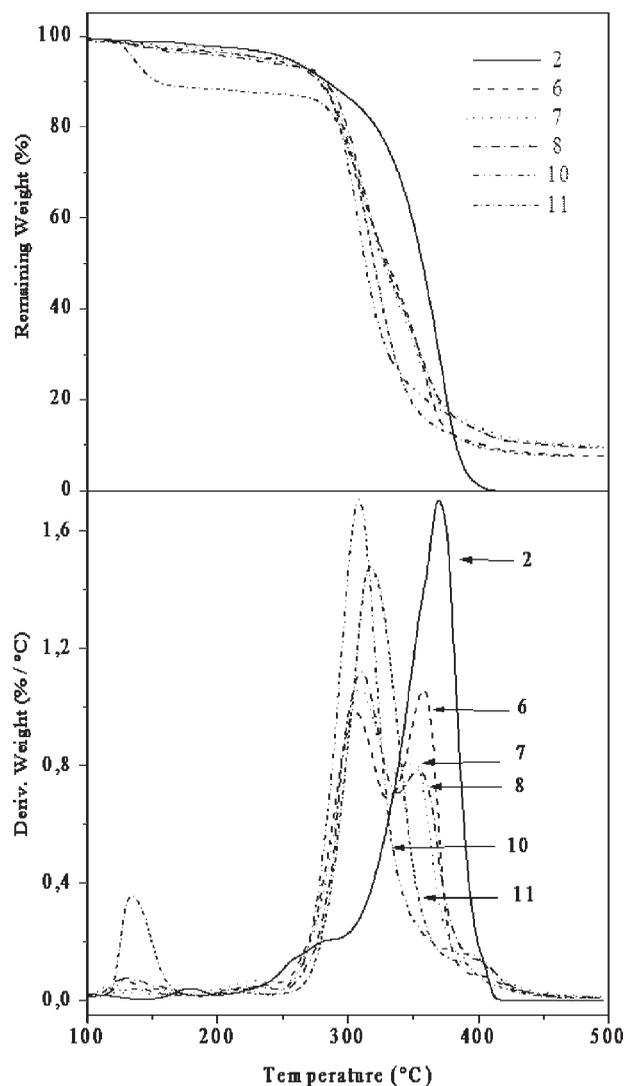


Figure 9 TGA and DTG curves of PMMA (2) and some MMA-4VP copolymers with different compositions (mol % of 4VP-unit as in Table I, entry 6–8 and 10–11).

one in the 300–400°C temperature range with a maximum at 369°C. The corresponding thermal degradation mechanism, in agreement with the literature data,⁴⁰ is promoted by the formation of long-chain polymer radicals from random chain scissions as well as initiation at an unsaturated chain end, whose undergo subsequent cleavage to product mostly MMA monomer. The copolymers underwent decomposition temperatures depend on copolymer composition and their T_{max} varied between 309 and 317°C, indicating obviously that the incorporation of 4VP into PMMA chains decrease its thermal stability. Besides, the copolymers of relatively low content of 4VP exhibit two-stage degradation behavior, while single step decomposition is observed for copolymers of relatively high 4VP content as for the P4VP degradation. Khairou and Diab⁴¹ have reported that the products of the thermal degradation of MMA-4VP copolymers were constituted mainly by the two monomers with traces of pyridine and 4-methylpyridine, suggesting that no interaction occurs between comonomer units during the degradation process.

Also, in the case of copolymers containing similar molar fraction of 4VP (entry 5 and 6), the enhancement in complex activity on going from C-1 to C-3 induced enhance in the maximum temperature of thermal decomposition about 18°C, hence an increase in copolymer stability.

CONCLUSIONS

Copolymers of MMA with 4VP have been successfully prepared at 30°C, using a novel Nickel(II)-Benzoinoxime complex, to yield appreciable molecular weights (10⁴ g/mol) with quite broad polydispersities values, indicating that copolymerization most probably proceeds via free radical mechanism. The

reactivity ratios of this pair of copolymers were estimated using linear graphical and nonlinear (RREVM) methods. In all cases, the r_v values were higher than the corresponding r_m and their product less than one indicating that a kinetic preference exists for a random incorporation of 4VP in copolymer chains. DSC study revealed that an increase of 4VP content in the copolymers led to a visible increase in T_g . The TGA showed that the stability of the copolymers decreases with increasing 4VP content. This study also revealed that the activity of the Ni complex towards polymerization reaction is greatly affected by its age.

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