Polymerization of Methyl Methacrylate with Nickel (II)α-Benzoinoxime Complex

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ABSTRACT: Polymerizations of methyl methacrylate (MMA) monomer initiated by a novel Ni(II)α-benzoinoxime complex have been achieved under homogeneous conditions in the 25–60°C temperature range. The activity for polymerization increases with reaction temperature and by carrying out the polymerization in solution of low-polarity solvents without any induction time. The obtained polymers have weight-average molecular weights about 10^5 and slight broad polydispersity indexes ($2.2 \leq M_w/M_n \leq 3.3$). Dependence of rate constants polymerization and decomposition of initiator (k_{app} and k_d, respectively) on temperature was investigated and activation parameters were computed from Arrhenius plot. ^{1}H-NMR analysis of PMMA revealed a syndio-rich atactic microstructure in agreement with conventional radical process. Radical scavenger TEMPO effect together with microstructure and molecular weight distributions data supported that the polymerization proceed via free radical mechanism. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1514–1522, 2008

Key words: radical polymerization; kinetics; microstructure, Ni(II); complex

INTRODUCTION

In recent years, polymerization mediated by transition metal complexes has gained an increasing interest.[1,2] For instance, Rh-based complex catalysts have been investigated because of their potential high reactivity, under mild conditions, toward the polymerization of monosubstituted acetylenes to give stereoregular polymers with high molecular weight and low polydispersity.[3,4] Thus, the polymerization of phenylacetylene (PA) proceeds rapidly to completion within 2 h in living manner, at room temperature, in the presence of cocatalysts.[5] Moreover, poly (propiolic acid) was produced in water at 30°C even in air.[6] On the other hand, some low spin Cobalt(II) complexes like cobaloximes[7] and bis[(difluoroboryl)-diphenyl gluoximato]cobalt(II),[8](CoPhBF), were found to be excellent regulators of average molecular weight of polymers through catalytic chain transfer polymerization of commercially monomers, such as methyl methacrylate (MMA) or styrene. The control of stereochemistry in free radical polymerization of maleimides was obtained using a chiral Cobalt(II)-complex.[9] Otherwise, organometal complexes were very successful (activators) in olefins activation polymerization via ATRP process. Thus, several classes of those catalytic systems based on Ni(II),[10] Fe(II),[11]

Ru(II),[12] Co(II),[13] and M_n(III)[14] have been reported to control the living radical polymerization of alkyl methacrylates or styrene in the 60–130°C temperature range as well as the synthesis of block,[15] functionalized, and multiarmed polymer.[16] Meanwhile, many efforts have focused on the polymerization of olefin monomers with nickel complexes.[17–19] The (α-diimine) Ni(II)/methylaluminoxane (MAO) catalyst system produced high-molecular-weight polymers with interesting physical properties.[20–22] A comparative study on the polymerization of MMA promoted by Mn(II), Ni(II), V(III), and Cr(III) complexed by the same ligand, acetylacetonate (acac) in presence of MAO, at 30°C, revealed that Ni(II) complex exhibits the highest catalytic activity.[23]

In this article, we have undertaken a study of MMA polymerization in solution using a newly developed nickel complex Ni(II)α-benzoinoxime as a single component initiator at different temperatures. Some of the advantages of this complex are its ability to mediate the polymerization in a homogeneous fashion at moderate temperature and its air stability and moisture absorption and can be handled even in open air.

We have investigated in this study, for the first time, both the kinetic features associated with the MMA polymerization in dioxane media using the above complex and its polymerization mechanism. The suggested process[24] for the formation of the Nickel complex (Scheme 1).

This study[24] showed that Ni(II) complex undergoes sluggishly oxidation to higher state Ni(IV) by
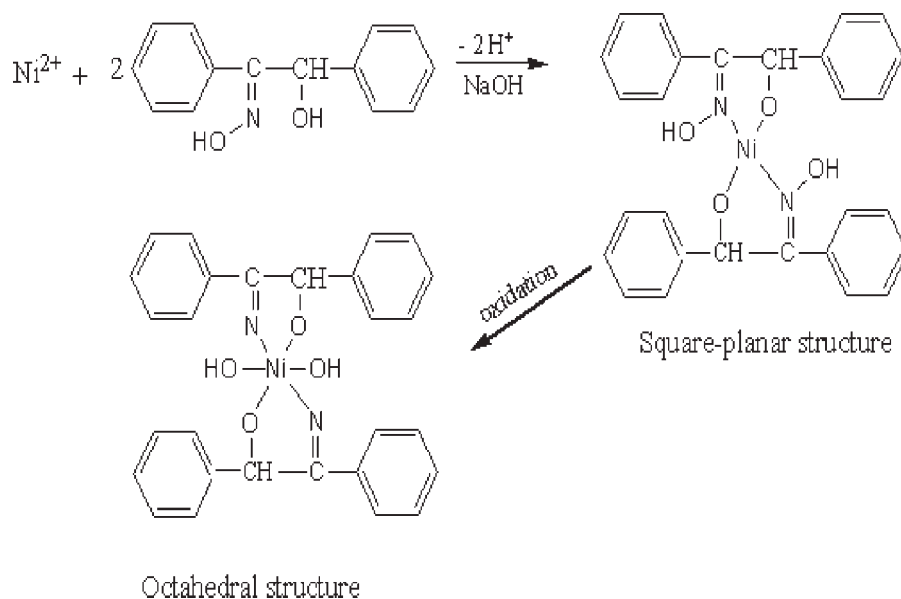
Scheme 1 Formation and suggested structure of Nickel(II)α-benzoinoxime complex.

the ligand in solid state, where an electronic exchange occurs between the metal and the ligand. This oxidation is accompanied by a structure change from square-planar to octahedral.

EXPERIMENTAL

Materials

MMA (Fluka, purity > 99%) was freed from inhibitors by distillation under reduced pressure. The middle fraction was collected and stored in a refrigerator before use. The Nickel(II) complex was prepared according to a standard procedure.[24] TEMPO (Aldrich, purity > 98%), dioxin, and methanol (purity > 99%) were used as received.

Polymerization procedures

Solution polymerization

The polymerization of MMA was carried out following a standard procedure: dioxan and MMA, in appropriate ratios, 60 and 80 mL respectively, were added to a round bottom flask equipped with stirring bar, and purged with Nitrogen for 20 min at room temperature. Subsequently, the reaction flask, maintained under nitrogen blanket, was immersed into a thermostated water bath at a selected temperature. As soon as the reaction mixture reached the desired temperature, complex solution, 8 mg in 20 mL of dioxan initially purged with Nitrogen is added to the flask with a degazed syringe. At timed intervals, samples were withdrawn from the flask using standard deaerated syringe technique and immediately precipitated in excess of methanol. The polymer was isolated by filtration, then washed with pure methanol, and dried in vacuum at 40°C to a constant weight. Monomer conversions were determined by standard gravimetric technique.

Bulk polymerization

Method 1. A 10 mL Schlenk flask charged with MMA, 5 mL, was deaerated three times by ''freeze-pump- thaw'' method, each cycle took 20 min, and sealed under vacuum. The flask was immersed in a water bath at a preset temperature, 30°C. The solid complex (5 mg) was added to the reaction flask as a dioxan solution, 0.1 mL, and degassed by purging with nitrogen before use, via nitrogen washed syringe. At the desired reaction time the flask was cooled to −195°C, opened, and exposed to air to stop the polymerization. The content was rapidly poured into a large amount of methanol to precipitate the formed polymer. The latter was collected by filtration, washed with methanol, and then dried under vacuum for several hours. Polymer yield was determined by gravimetry.

Method 2. Polymerization was carried out by the syringe technique under nitrogen in Schenk tube. In 10 mL Schlenk tube, 3 mg of complex is degassed by nitrogen for at least 1 h. An amount of 3 mL of MMA, previously deaerated with bubbling nitrogen for the same time, is added by syringe and then placed in a 30°C thermostated water bath. The reaction mixture was homogeneous.

Determination of molecular weight average M_n, M_w and polydispersities of polymers were effectuated by size-exclusion chromatography (SEC) in THF at 23°C with a Waters GPC II liquid chromatograph.
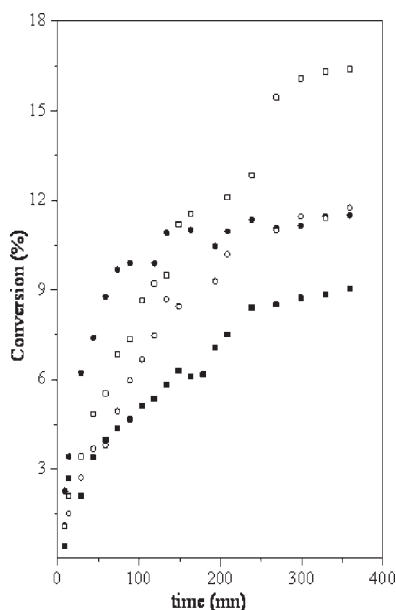
Figure 1 Conversion-time profile for MMA polymerization in presence of Ni(II)α-benzoinoxime complex at temperatures (°C): 25 (■), 30 (●), 40 (○), and 60 (□).

The columns were connected to Model 590 pump and Differential refractometer R401 detector, and calibrated against standard poly(methyl methacrylate) samples. Molecular weights, M_v, of PMMA samples were determined by viscometry. The M_v value was determined according to Mark-Houwink-Sakurada eq. (1) with $K = 7.7 \times 10^{-2}$ mL/g and $a = 0.65$ at 30°C for the PMMA/Dioxan system.[25]

$$[\eta] = K(M_v)^a \tag{1}$$

The intrinsic viscosity $[\eta]$ previously determined at 30°C.

The ^{1}H-NMR Spectra of the polymers were recorded in CD_2Cl_2 at 25°C on a Bruker AM 300

spectrometer, operating at 300.13 MHz, with TMS as reference. The UV–vis spectra of polymers were recorded on a Perkin-Elmer Lamba-20 spectrometer.

RESULTS AND DISCUSSION

Polymerization of MMA with Ni(II)α-Benzoinoxime complex

The results of MMA solution polymerization, [dioxan/monomer = 1 : 1(v/v)] with Ni(II)α-benzoinoxime complex at different temperatures are depicted in Figure 1 and summarized in Table I. As it can be seen, the nickel complex is found to be active for the polymerization of MMA in the investigated temperature range 25–60°C and even at 4°C, in a sharp contrast to many other catalysts such as, Co(acac)$_2$ that alone proved to be inactive for MMA polymerization.[26] Also, the use of Rh[(norbornadiene) Cl]$_2$ complex in conjunction with suitable cocatalyst induced instantaneous polymerization of PA while no polymer was formed without the cocatalysts.[27] It is worthwhile to mention that in all cases polymerization proceeds in absence of any induction times. In fact, monitoring the conversion in time for several temperatures shows that it increases until it reaches a nearly level off attributed to monomer concentration limit $[M]_\infty$ corresponding to the maximum possible conversion. This critical value is determined by the extrapolation of the tangent in this region of plot. Moreover, the yields increased steadily with raising temperature, but no gel effect occurred that should indeed lead to a sharp increase of the conversion.The Ni(II)α-benzoinoxime has however only a moderate activity for polymerization even at the highest reaction temperature: about 16% conversion for 6 h at 60°C as compared to free radical conventional initiator like AIBN. In the contrary, lower conversions were observed at higher temperatures in MMA polymerizations mediated by both vanadium

TABLE I
Polymerization of MMA Mediated by Ni(II)α-Benzoinoxime Complex in Dioxan at Various Temperatures[a]

Temperature (°C)	Time (h)	Yield (%)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	$M_v \times 10^{-5}$	M_w/M_n
4	77	6.52	–	–	–	–
25	3.5	7.48	0.946	3.117	–	3.295
25	4.5	8.48	–	–	0.588	–
25	6.0	8.99	1.00	3.342	–	3.334
30	3.5	10.93	0.443	0.895	–	2.021
30	4.5	11.05	–	–	0.868	–
40	3.5	10.28	1.519	4.772	–	3.141
40	4.5	10.96	–	–	1.00	–
40	6.0	11.72	2.201	4.999	–	2.271
60	3.5	12.06	1.509	4.111	–	2.858
60	4.5	15.40	–	–	1.587	–
60	6.0	16.35	2.608	5.873	–	2.252

[a] Polymerization conditions: MMA/dioxan (1/1 vol ratio), MMA/complex (1/10^{-3} mass ratio).

TABLE II
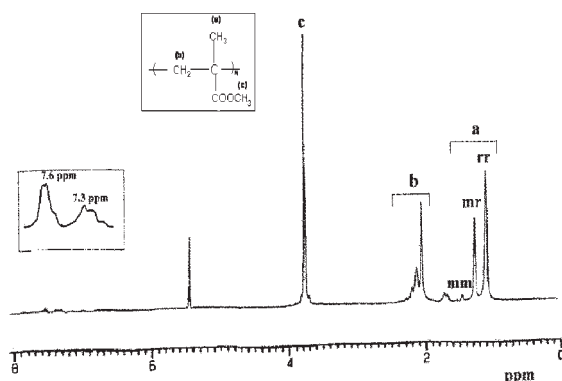**Polymerization of MMA with Ni(II)α-Benzoinoxime Complex at 30°C in Several Solvents for 6 h[a]**

Solvent	Yield (%)
DMF	Trace
Acrylonitrile	Trace
Cyclohexanone	0.83
THF	8.04
Dioxan	10.72

[a] In all cases: MMA/solvent (1/1 vol ratio), MMA/complex ($1/10^{-3}$ mass ratio).

based catalysts $V(acac)_3$ and $VOCl_3$ in combination with MAO[28] and bis(cyclopentadienyl) titaniumdichloride, (Cp_2TiCl_2), complex.[29] Undertaken studies focused on improving the yields of MMA polymerizations by addition of additives (accelerator) as well as Et_3N led to a remarkable enhancement. Indeed, the polymer yield reached about 16.5% when molar ratio Et_3N/Ni value was 282 under the same experimental conditions at 25°C for 4 h. This investigation is now in progress.

The effect of solvent polarity was examined on the polymerization and the results are shown in Table II. It is clear that the monomer conversion depressed with increasing solvent polarities. Thus, when highly-polar solvent such as DMF was used in polymerization, the polymer yield was insignificant. In contrast, the dioxan a less polar solvent has been shown to be the best solvent for the polymerization of MMA.The same MMA polymerization trend induced by $Ni(acac)_2/MAO$ system was observed.[30] Consequently, this latter solvent was employed exclusively in our experiments.
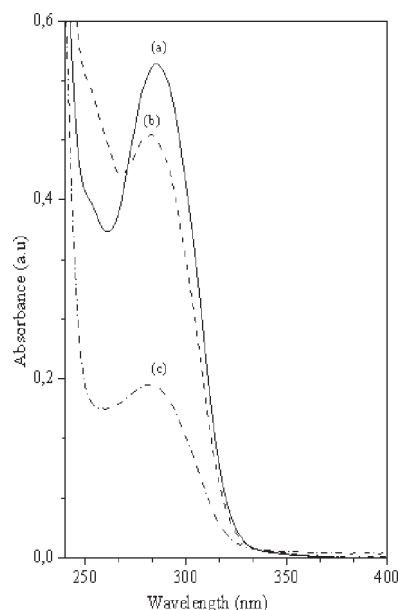
It is also noteworthy that the bulk polymerization of MMA is very sluggish and hardly proceeds with Ni(II)α-benzoinoxime complex at 30°C contrary to the conventional free radical initiator. In fact, the polymer yield dropped from 11% (solution process)
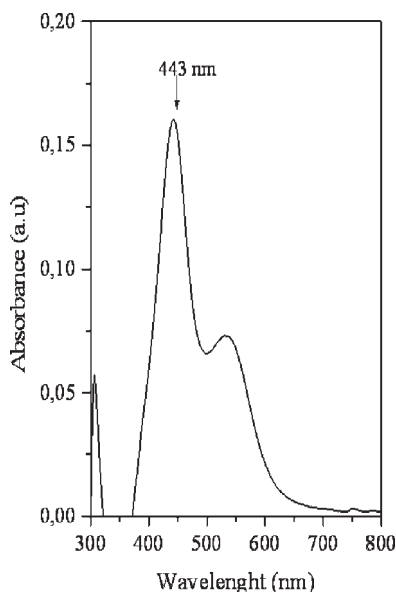
to less than 1.5% for 4 h. The same behavior was observed in styrene polymerization initiated by Ni(II) based acetylide complex $Ni(C\equiv CPh)_2$ $(PBu_3)_2$.[31] The obtained results suggest, though not enough to prove, that dioxan as used at 50% (v/v) increases the nickel activity toward the MMA polymerization by an increase of the rate of initiation, in agreement with those reported in free radical polymerization of acrylonitrile initiated by $Mn(acac)_3$.[32] Studies to clarify this aspect are in progress.

^{1}H-NMR analysis of PMMA was performed, in particular, to throw light on the nature of the initiating species by detecting the end-groups of the resulting polymer. As can be seen from Figure 2, the aromatic range of 7–8 ppm shows two weak signals related to the phenyl group. Because of low amount phenyl containing component bound to polymeric chains a reliable integration could not be obtained. This finding is confirmed by UV detection of isolated and concentrated homopolymer samples obtained at several temperatures, Figure 3. Indeed, both spectra show an absorption maximum at 283 nm ascribed to $\pi \rightarrow \pi^*$ transition conjugated phenyl decreasing with an increase of temperature. These results indicated unambiguously the incorporation of active initiating species in polymer chain that could arise from the complex as well as the ligand obtained after decomplexation of Nickel complex.To check this point, two experiments were designed. First, blank experiments showed that α-benzoinoxime alone had no activity toward MMA polymerization. On the other hand,

Figure 2 ^{1}H-NMR spectrum of PMMA obtained with Ni(II)α-benzoinoxime complex initiator in D_2CCl_2.

Figure 3 UV spectra of poly(MMA) obtained with Ni(II)α-benzoinoxime complex, in chloroform at equal concentrations (4 g/L), for 5 h at temperatures (°C): 25 (a), 30 (b), and 60 (c).
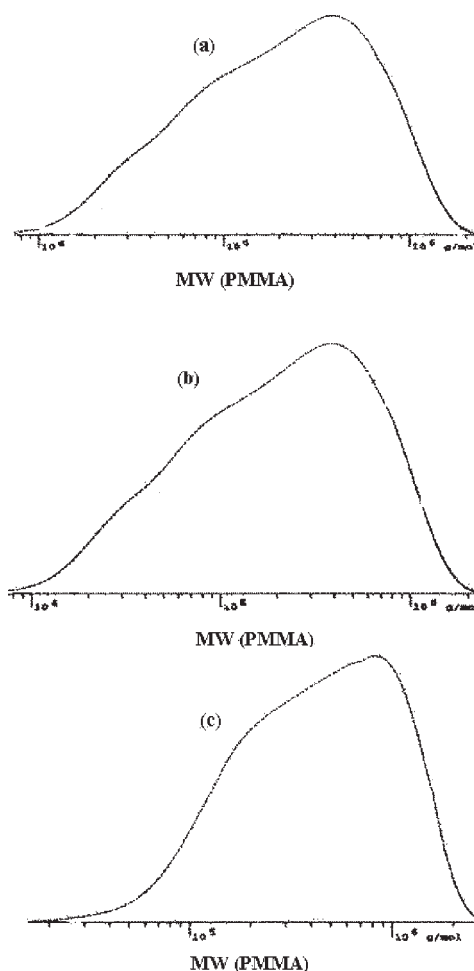
Figure 4 Visible spectrum of Ni(IV)dimethylglyoxime complex in oxidizing medium.

suppressed in free radical process and became prominent the longer the reaction proceeds, leading to significant amount of dead chain ends. Surprisingly, with raising polymerization temperature the values of M_n, M_w, and M_v increase fairly accompanying slightly decrease of polydispersity. This is evidenced from a UV analysis that showed a decrease of the initiation efficiency of the initiator with temperature. In other words, a long lived propagating chains and hence higher molecular weights. Similar observations are made for the polymerization of 1,3-butadiene with Co(acac)$_3$ in combination with MAO.[34] Despite the best activity of Ni(acac)$_2$/MAO catalyst system toward the polymerization of MMA (31.7% monomer conversion at 30°C for 5 h), polymers with low molecular weight, 6.10^3, and a rather high polydispersity of 4.61, were achieved.[23] Despite the broadening of the molecular weight distribution, no gel effect was observed because this phenomenon takes place at higher conversion (up to 40%) in monomer

thermal gravimetric analyses of Nickel metal derived from complex were performed on a large amount of polymer. When PMMA sample (11 g) was introduced into an oven heated up to 800°C for 2 h, instantaneous combustion was observed and a small residual black product was collected indicating presumably the formation of oxide of Nickel at this temperature.

For a further characterization, the Nickel from oxide was removed by dissolution in acidic medium (HNO$_3$) followed by colometric titration using dimethylglyoxime (DMG) according to a literature procedure.[33] Evidence of Nickel-DMG complex ($\varepsilon = 13{,}740$ mol^{-1} L cm^{-1}) was observed by UV–vis analysis that displays a maximum absorption at 443 nm attributed to d → d transition, Figure 4. This analysis led to about 0.008% content of metal in PMMA.It appears to be plausible and most straightforward to assume that the complex is the candidate for initiating polymerization of MMA.

GPC analyses and viscometry measurements of the polymers prepared with Ni(II)α-benzoinoxime are shown in Table I. As it can be seen, the molecular weights of PMMA are above 10^4. Also, polydispersity values were quiet high ($2.2 < M_w/M_n < 3.3$ for 6 h) and are close to those resulting from free radical polymerization process, supporting that Ni(II)α-benzoinoxime complex exhibits a free radical behavior in the temperature range of 25–60°C. Correspondingly, MWD obtained are substantially broad regardless of the polymerization temperature, Figure 5. This is presumably because of the fact that irreversible termination reactions cannot be completely

Figure 5 MWD chromatogram curves of poly (MMA) obtained with Ni(II) α-benzoinoxime complex in dioxan for 6 h at temperatures (°C): 25 (a), 40 (b), and 60 (c).
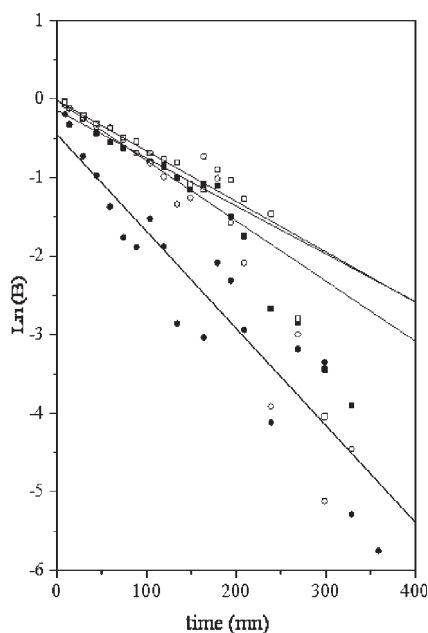
Figure 6 Kinetic plots of decomposition of Ni(II)α-benzoinoxime complex in MMA solution polymerization at various temperatures in °C: 25 (■), 30 (●), 40 (○), and 60 (□).

concentrated solutions or in a bulk process. In all our experiments, conversions did not exceed 17%.

Kinetic studies

Kinetic parameters of MMA polymerizations promoted by Ni(II)α-benzoinoxime are discussed by analogy to conventional radical initiator such as AIBN. These values were derived from "classical free radical polymerization" model.

Under these considerations the decomposition constant k_d (s^{-1}) constant can be expressed as in eq. (2).

$$B = \exp((-k_d/2)t) \qquad (2)$$

with $B = (Ln[M]_\infty - Ln[M]_t)/(Ln[M]_\infty - Ln[M]_0)$ where $[M]_0$, $[M]_t$, and $[M]_\infty$ are the concentrations monomer for t_0 (initial time), t (any time), and t_∞ (limit conversion).

The slopes of the linear plots of Ln(B) = f (time) yields $k_d/2$, and hence k_d values at different temperatures, Figure 6 and Table IV. The apparent rate constant polymerization, k_{app} (s^{-1}) may be determined via linear regression analysis of the experimental data according to eq. (3).

$$Ln([M]_0/[M]) = k_{app}t \qquad (3)$$

Correspondingly, activation energies of polymerization were evaluated from the Arrhenius plot of k_d

and k_{app} data, as pointed above at four temperatures, accordingly to eq. (4).

$$k_x = A \exp(-E_x/RT) \qquad (4)$$

where $k_x = k_d$ or k_{app} and $E_x = E_d$ or E_{app}.

The representative results from kinetic studies are depicted in Figures 6–8 and summarized in Table IV. Apparently, the polymerization of MMA is well described as being first order in time conversion irrespective of polymerization temperature, Figure 6. Also, curves closely coincide with one another up to $t \approx 200$ min, beyond which negative deviations from the linearity become apparent. Thus, the values of k_d would be best estimated at an early stage of polymerization. The values of k_d obtained within this temperature interval are about 10^{-4}(s^{-1}) and the corresponding activation energy, E_d, given in Figure 8, is determined to be 1.107 kJ Mol^{-1}, Table IV. The low energy of activation can be interpreted as a consequence of a high catalytic activity of the complex in the initiation step. It should be emphasized that despite its lower activation energy, the k_d values of this initiator are larger than those of several commonly used radical initiators such as AIBN at 60°C (k_d = 8.5 0 × 10^{-6} s^{-1} and E_d = 123 kJ mol^{-1}).[35] A good agreement of these values is however observed at 80°C (k_d = 1.49 × 10^{-4} s^{-1}).This result is not surprising because the polymerization occurred even at
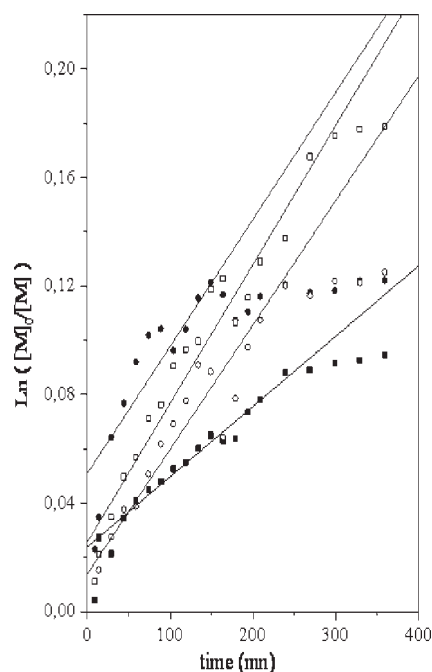
Figure 7 Semilogarithmic kinetic plots for the polymerization of MMA with Ni(II)α-benzoinoxime complex in dioxan at various temperatures in °C: 25 (■), 30 (●), 40 (○), and 60 (□).
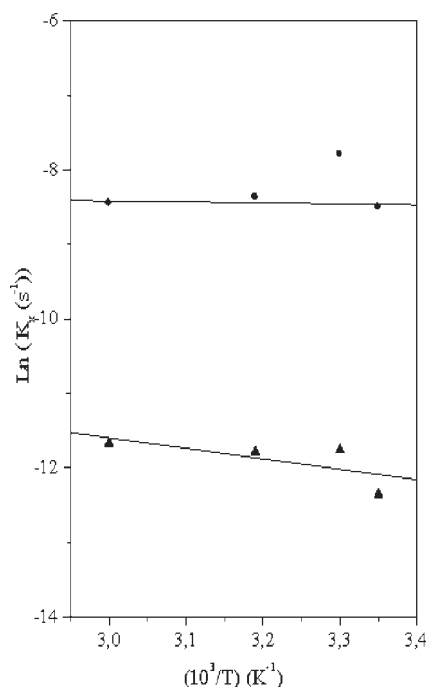
Figure 8 Arrhenius plots for the polymerization of MMA in dioxan initiated by Ni(II)α-benzoinoxime complex: k_d (●), k_{app} (▲).

TABLE III
Triad Tacticity of PMMA Obtained with
Ni(II)α-Benzoinoxime Complex at Various Temperatures
as Determined by ¹H-NMR for 3.5 h

Temperature (°C)	Tacticity (%)		
	mm	mr	rr
25	3.84	31.23	64.93
30	2.69	32.55	64.76
40	3.65	35.50	60.85
60	4.18	35.36	60.46

nism such as AIBN (85 kJ Mol^{-1}) and photochemical polymerization (20–30 kJ Mol^{-1}).[36]
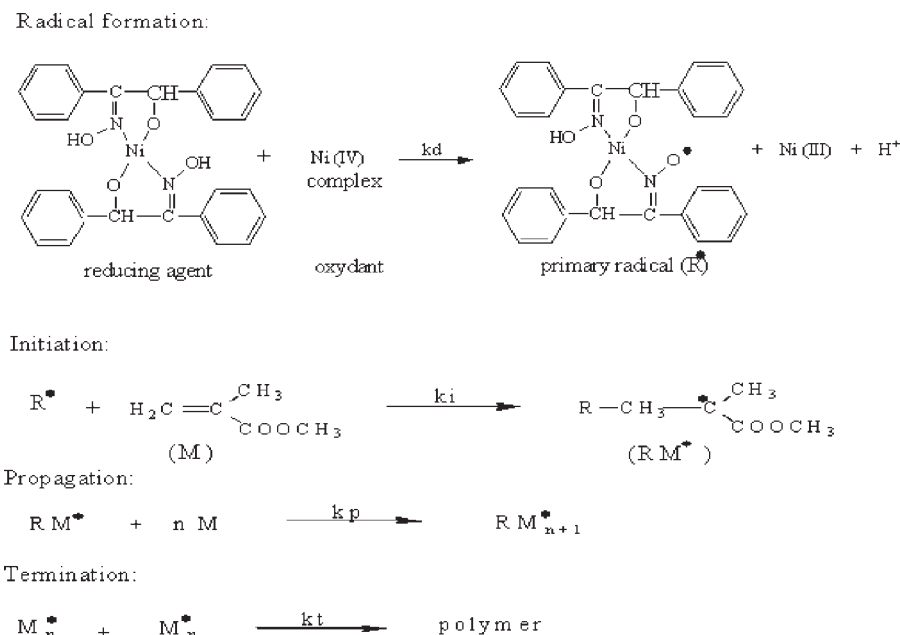
Stereochemistry

¹H-NMR analysis of the polymers gave support to the nature of polymerization process, as already out lined. Indeed, as pictured in Figure 2, the obtained polymers had a syndio-rich atactic microstructure in agreement with that of PMMA free radically prepared by conventional initiator like AIBN.[28] The stereoregularities were calculated from the α-methyl resonance triplet in the region 0.8–1.3 ppm. The relative intensities of the three triads α-methyl group provide a measure of the triad percentages mm, mr, and rr, Table III. These polymers have the same tacticity as those reported for both the conventional radical polymerization and the ATRP process.[37–39] Although highly stereoregular polymers were not obtained with this complex, the isotactic triads mm of the polymers enhance slightly with polymerization temperature.

Mechanism

To shed more light on the nature pathway of this polymerization, we have considered the effect of typical true radical scavenger additive, for instance, TEMPO on the polymerization of MMA with Ni(II) α-benzoinoxime in dioxan at 75°C. Two experiments were performed. In the first one, the polymerization was allowed to proceed to 20% conversion in absence of additive for 6 h. In the second one, 1.5 molar equiv of TEMPO was added into the medium

low temperature (4°C) as evidenced by conversion data shown in Table I.

Figure 7 shows the plot of Ln([M]$_0$/[M]) versus time, of the polymerization of MMA in dioxan at various temperatures. As it can be seen, this process is first order with respect to time conversion up to 200 min, beyond which occurs a more pronounced deviation at all temperatures. Such behavior is in general due to the occurrence of physical effects, i.e., to the increase of viscosity of the polymerization as the reaction proceeds. However, our experiments are carried out in solution without any significant physical effects. Thereby such deviation might arise from permanent deactivation, e.g., inherently easy radical chain termination reactions, i.e., recombination and disproportion which are important in conventional radical polymerization of MMA.[36] Otherwise, the linearity of semilogarithmic scale, before 200 min, reveals that the concentration of growing species throughout polymerization remains constant. Moreover, the straight lines passing nearly through the origin indicated that no induction time occurs. The slope of the plots in Figure 8 allows the calculation of k_{app} values represented in Table IV. Remarkably, these values (10^{-6} s^{-1}) close to that of AIBN at 60°C increase slightly with temperature. The activation energy is determined from the plots of the apparent rate constants k_{app}, Figure 8. The resulting E_{app} value of 11.67 kJ Mol^{-1} is not consistent with those obtained with free radical polymerization mecha-

TABLE IV
Kinetics Parameters of MMA Polymerization Promoted
by Ni(II)α-Benzoinoxime Complex

Temperature (°C)	$k_{app} \times 10^6$ (s^{-1})	$k_d \times 10^4$ (s^{-1})	E_{app} (kJ mol^{-1})	E_d (kJ mol^{-1})
25	4.319	2.03		
30	7.812	4.116	11.671	1.107
40	7.652	2.310		
60	8.541	2.140		

Radical formation:

Initiation:

Propagation:

Termination:

Scheme 2 Proposed mechanism of MMA polymerization initiated by Ni(II)α-benzoinoxime complex.

after the polymerization had reached 8% conversion of MMA for 3 h. Upon addition of TEMPO, no further polymerization occurred beyond as evidenced by the virtual absence of conversion increase for prolonged time. This indeed affected the progress of monomer consumption. Once again, these results strongly support the occurrence of radical process. Thus, generation of free radicals from complex and their initiation ability were investigated. Several polymerization runs were carried out with freshly synthesized 5-day-old or 3-year–old complex, under the same tested conditions. No activity of both complexes was found within 6 h. This may probably be due to the oxidative effect of ligand toward the metal center in the complex aforementioned. Indeed, in the former case, the Ni(IV) complex obtained from Ni(II) complex was not yet formed and therefore this later cannot mediate polymerization. In the second case, the disappearance of the Ni(II) complex by oxidation into Ni(IV) complex was complete. Consequently, the initiation mechanism requires presumably the contribution of both species simultaneously in the solid state complex.

By analogy with redox initiation, a very effective method of generating free radicals under milder conditions than thermal polymerization by single-electron transfer process, we believe that both Ni(IV) and Ni(II) complexes are involved in initiation mechanism as redox pairs.

Similarly as reported by Sarac,[32] it was generally suggested that redox initiation systems involve reducing agents such as alcohols, thiols, amines in combination with oxidizing metal ion at higher valent. The Ni(II) complex acts not only as reducing agent but also as a generator of radicals which are intercepted by the initiation of polymerization. Ni(IV) chelate, used as oxidant, is strong enough to split the O—H bond of oxime function in Ni(II) complex.

Accordingly, Ni(IV) species promote an homolytic cleavage of the previous bond yielding free radical initiating species. This breakdown is accompanied by direct electron transfer from reducing agent to Ni(IV) metal center. The propagation takes place though successive addition of monomers to growing polymer chains that were terminated by the mutual annihilation of polymer radicals. The proposed mechanism steps are depicted in Scheme 2.

CONCLUSIONS

This study has thus enlarged the scope of transition metal complex as active initiator usable even around room temperature. Indeed, the polymerization of MMA can be triggered by Ni(II)α-benzoinoxime yielding polymers with weight-average molecular weight of about 10^5 and reasonable polydispersities. The conversion increases with temperature together with a slight increase in molecular weights (M_n, M_w) and a slightly broader molecular weight distribution. Moreover, the complex exhibits a very poor activity in bulk process or in high polarity solvents. GPC and NMR analysis together with the additive TEMPO effect indicated that the complex displayed free radical characteristics. From kinetic studies, the apparent polymerization rate constants k_{app} show a good correspondence with those deter-

mined in MMA polymerization promoted by AIBN, while the activation parameters are somewhat lower. Otherwise, the initiation step seems unaffected by an increase of temperature. Moreover, a plausible redox initiation mechanism of MMA polymerization is also presented.

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