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Controlled Radical Polymerization of Methacrylic Monomers in the Presence of a Bis(ortho-chelated) Arylnickel(II) Complex and Different Activated Alkyl Halides

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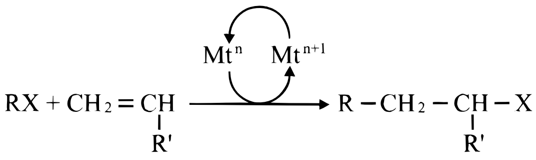
ABSTRACT: A novel class of homogeneous nickel(II) catalysts, i.e [Ni{*o*,*o*′($CH_2NMe_2)_2C_6H_3$}Br], denoted as Ni(NCN′)Br, is reported to mediate in the presence of activated alkyl halides, e.g., CCl_4 or α-halocarbonyl compounds, a well-controlled radical polymerization of methacrylic monomers [methyl and n-butyl methacrylate), (MMA, n-BuMA)] at rather low temperatures (<100 °C). The number-average molecular weight of the polymer gradually increased with the monomer conversion and was inversely proportional to the initiator concentration of alkyl halides. The molecular weight distribution (MWD) remained very narrow during the whole course of the polymerization (MWD < 1.3). All the experimental data including a successful block copolymerization (*n*-BuMA-*b*-MMA) experiment were in agreement with a living polymerization process, and remarkably enough, poly(methyl methacrylate) (PMMA) with molecular weight up to at least 10^5 g/mol was synthesized in a controlled fashion. Increased thermal stability of the PMMA is a further indication of the high regioselectivity and the virtually absence of termination reactions. Owing to the compatibility of the Ni(II) complexes toward water, extension to aqueous suspension polymerization was attempted successfully as attested by the promising preliminary results. Indications on the mechanism let us suggest that the reactive alkyl halide or the corresponding growing chain end is reversibly activated/deactivated by single electron transfer together with the halogen transfer.

Introduction

Because of high chemoselectivity and regioselectivity, living polymerization is among the best methods to prepare polymers with controlled molecular weight and well defined chain end structure. In anionic and cationic living and/or controlled polymerization, chain growth occurs indefinitely without transfer and termination reactions.[1] However, all these polymerization processes strongly suffer from their sensitivity toward a number of agents, particularly hydrogen-active compounds such as water.

Free radical polymerization can be readily performed in bulk, aqueous emulsion or suspension. Compared to ionic processes, it also takes advantage of its ability to polymerize a wider variety of monomers. On the other hand, chain growth is still very difficult to control because of the high reactivity or low stability of radicals, which leads to transfer or to fast irreversible termination reactions via coupling and/or disproportion. Moreover, termination is a second-order reaction while propagation is first-order in active centers; therefore, the probability of termination is favored with increasing concentration of growing chains.

In the recent years, several research groups[2−11] have focused on this problem, and a concept based on reversible termination of growing radicals has been successfully developed in a number of systems. As a result, polymers with predetermined molecular weight, narrow polydispersity, functional end groups, and complex architectures have been obtained and characterized.



$$\mathrm{RX} + \mathrm{CH_2{=}\underset{\displaystyle R'}{CH}} \xrightarrow{\mathrm{Mt}^{n}\ \rightleftarrows\ \mathrm{Mt}^{n+1}} \mathrm{R{-}CH_2{-}\underset{\displaystyle R'}{CH}{-}X}$$

More recently, as an extension of the metal-catalyzed Kharasch addition of (poly)haloalkanes to alkenes (eq 1), Sawamoto et al.[10] first reported that methyl methacrylate was polymerized homogeneously in toluene at temperatures ranging from 60 to 80 °C in the presence of $CCl_4/RuCl_2(PPh_3)_3$ or α-halocarbonyl/$RuCl_2(PPh_3)_3$ and a Lewis acid as activator. All of the experimental criteria of a living polymerization were fulfilled. Shortly thereafter, Wang and Matyjaszewski described a living/controlled bulk polymerization of styrene at 130 °C in the presence of a 1-phenylethyl chloride/CuCl/2,2′-dipyridyl system.[11a] Later, the polymerization with RX/CuX (X = Cl, Br) was extended to other monomers such as (meth)acrylates.[11b]

Ruthenium and copper polymerization systems seem to proceed by the same reversible redox mechanism in which the alkyl (RX) or polymeric ($R(M)_pX$) halides are repeatedly activated by the transition metal species Mt^n to form the growing radicals $R(M)_p°$ and a Mt^{n+1} complex which can further react in a reversible transfer process to regenerate Mt^n and $R(M)_pX$. The catalyst thus acts as a halogen carrier, allowing controlled step growth to proceed by repetitive addition.

Besides those ruthenium and copper complexes, other redox systems based on low valency metal carbonyl complexes and polyhalogenomethanes had been used as initiators for radical polymerization, but none of them exhibited the living polymerization criteria.[12]

In this study, we wish to report a novel class of homogeneous nickel(II) catalysts, i.e [Ni{*o*,*o*′-($CH_2NMe_2)_2C_6H_3$}X] (X = Br), denoted as (Ni(NCN′)Br, which provides controlled polymerization of methacrylic monomers in the presence of different activated alkyl halides at temperatures below 100 °C. Moreover, tolerance of this family of complexes toward water allows an evaluation of their capacity to induce polymerization in aqueous medium.

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Experimental Section

Materials. MMA (methyl methacrylate) and n-BuMA (*n*-butyl methacrylate) from Aldrich were distilled from CaH_2 and then stored under nitrogen atmosphere at −20 °C. Toluene was purified by refluxing over CaH_2 and then sodium under nitrogen for several days and freshly distilled and bubbled with dry nitrogen for more than 15 min immediately before use. THF was refluxed over Na/benzophenone complex for several days, and freshly distilled and bubbled with dry nitrogen before use. Bis(ortho-chelated) aryldiaminenickel(II) complex was prepared according to the procedure of Van Koten et al.[16] with Aldrich materials, and $Ni(COD)_2$ was obtained from Strem Chemicals. CCl_4 and α-halocarbonyl (Aldrich) compounds were used without any further purification.

Polymerization. The polymerizations were carried out in glass tubes previously degassed under vacuum. Alkyl halides in toluene solutions, monomer, and catalyst solutions (toluene) were transferred by syringes and stainless steel capillaries under nitrogen. Three freeze−pump−thaw cycles were performed to remove molecular oxygen from the polymerization mixture, afterwhich the tubes were sealed under vacuum and placed in an oil bath held by a thermostat at the desired temperature. Since most of the reactions were performed almost in bulk, the content of the tubes completely solidified and stirring was inhibited when conversion reached about 50%. Polymerizations were stopped by cooling the tubes into liquid nitrogen. Afterward, the tubes were opened and the contents dissolved in THF. The PMMA [poly(methyl methacrylate)] was recovered by precipitation in methanol or heptane, filtered, and dried under vacuum at 60 °C overnight. The metal-containing residues were removed during precipitation and by washing the polymer with an excess of methanol. Conversions were calculated gravimetrically.

However, polymers corresponding to the kinetics experiments were evaporated to dryness to calculate conversions. Catalyst was removed by passing a polymer solution in THF through activated Al_2O_3 before characterizations.

Polymerization in an aqueous suspension of MMA (23 wt %)was carried out in the presence of sorbitane monooleate poly(ethylene glycol) (20) (Tween 80, 1 wt %, from I. C. I. Co.).

Characterizations. ^1H NMR spectra were recorded in $CDCl_3$ with a Brucker AM 400 apparatus at 25 °C. Size exclusion chromatography (SEC) was performed in THF at 40 °C using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index and UV detectors. Columns were calibrated with PMMA standard samples. TGA measurements were carried out under nitrogen flow by using a Dupont TGA 51 thermogravimetric analyzer (heating rate = 10 °C min^{-1}).

Results and Discussion

It was reported[13] that square planar organonickel(II) amine species $[Ni\{C_6H_3(CH_2NMe_2)_2\}X]$ (X = Cl, Br, I) were among the most effective complexes so far identified for achieving the homogeneous catalytic Kharasch addition of perhaloalkanes onto MMA. Further studies[14,15] indicated that involvement of carbon centered radicals was almost certain via an innersphere pathway. The intimate metal centered mechanism might thus explain the high regioselectivity in the final 1:1 adduct.

These results prompted us to synthesize Ni(NCN′)Br according to the literature procedure[16] and evaluate it first in MMA polymerization.

(a) Polymerization of MMA Promoted by Ni(NCN′)Br/Carbon Tetrachloride (CCl_4). In order to examine the influence of each component, (Ni(NCN′)Br and CCl_4, reactions were performed in toluene at 80 °C under various experimental conditions as summarized in Table 1. Without Ni(NCN′)Br or CCl_4, conversions are low or even nil after 22 h and polymers have ill-controlled molecular weight (MW) and broad molecular weight distribution (MWD). However, with the homogeneous binary initiating system Ni(NCN′)-Br/CCl_4, MMA conversion reaches 80% and the polymer thus obtained has a very narrow MWD (M_w/M_n < 1.2). The mean degree of polymerization (DP_n) is predetermined by the molar ratio of monomer to CCl_4, so CCl_4 is considered to act as initiator. These results illustrate the importance of both nickel complex and CCl_4 for a successful polymerization process.

Table 1. MMA Polymerization in Toluene with Various Components at 80 °C[a]

entry	$[CCl_4]_0 \times 10^2$ (mol/L)	$[Ni(NCN')Br]_0 \times 10^2$ (mol/L)	% yield	M_n[b] (g/mol)	M_w/M_n[b]
1	2.85	9.4	80	12 300	1.2
2	0	9.4	15	245 000	3.1
3	2.85	0	trace		

[a] Conditions: $[M]_0$ = 6.7 mol/L; polymerization time = 22 h. [b] After precipitation in MeOH, calculated from GPC, using PMMA standard samples.

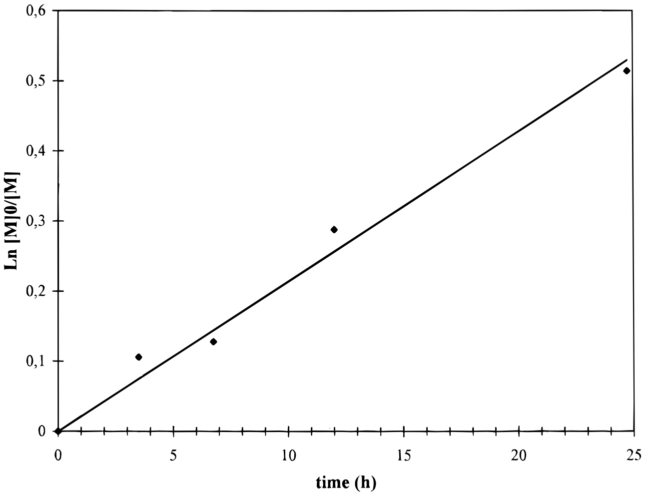

Figure 1. First-order plot of the $\ln[M]_0/[M]$ versus time (hours) for MMA polymerization in toluene at 74 °C in the presence of CCl_4/Ni(NCN′)Br: $[MMA]_0$ = 8.15 M; $[CCl_4]_0$ = 16.7 mM; $[Ni(NCN')Br]_0$ = 40.6 mM.

The kinetic plot of the polymerization initiated by CCl_4/Ni(NCN′)Br at 74 °C is shown in Figure 1. The polymerization medium solidified after 50% conversion because of a reaction temperature lower than the glass transition temperature of the PMMA. Therefore, the reaction was stopped before this point was reached. The linear semilogarithmic plot of $\ln([M]/[M]_0)$ versus time indicates that polymerization is first-order with respect to monomer and that the concentration in active centers remains constant throughout the polymerization. This already suggests that no termination reactions occurred during the polymerization process. The number-average molecular weight (M_n) increases gradually with monomer conversion (Figure 2), and the MWD of crude polymers as recovered without precipitation in methanol remains narrow all along the course of polymerization (Figure 3). At, for example, 40% conversion, the MWD is 1.16. However, some deviation from the theoretical M_n was observed. Sawamoto et al.[10] reported a similar behavior for the polymerization of MMA initiated by $CCl_4/RuCl_2(PPh_3)_3/MeAl(ODBP)_2$ in toluene at 60 °C. Studies concerning this deviation are in progress. Furthermore, a successful monomer-resumption experiment was carried out. To PMMA ($M_{n,exp}$ = 12 300 g/mol, M_w/M_n = 1.16, conversion = 80%, time = 22 h) synthesized in toluene at 80 °C was added a second identical fresh MMA feed into the solidified system and a 85%

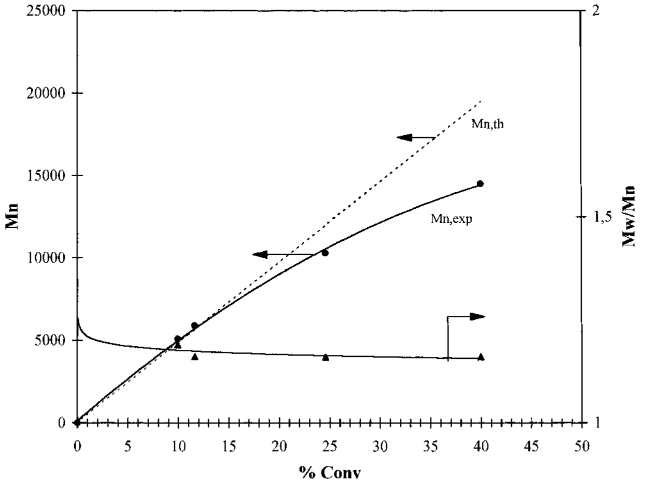

Figure 2. Dependence of M_n on conversion for MMA polymerization in toluene at 74 °C in the presence of CCl_4/Ni(NCN′)-Br: $[MMA]_0 = 8.15$ M; $[CCl_4]_0 = 16.7$ mM; $[Ni(NCN')Br]_0 = 40.6$ mM.

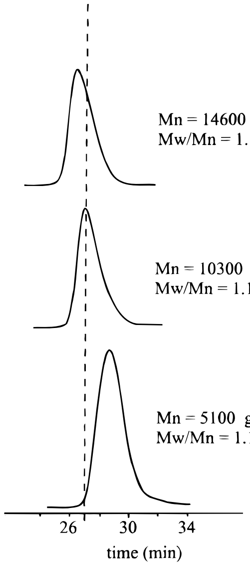

Figure 3. Evolution of the molecular weight distribution, M_w/M_n, with monomer conversion for MMA polymerization in toluene at 74 °C in the presence of CCl_4/Ni(NCN′)Br: $[MMA]_0 = 8.15$ M; $[CCl_4]_0 = 16.7$ mM $[Ni(NCN')Br]_0 = 40.6$ mM.

Table 2. MMA Polymerization in Toluene Initiated with Ni(NCN′)Br/2-(EiB)Br[a]

entry	$[RX]_0 \times 10^2$ (mol/L)	Ni/RX[b]	time (h)	temp (°C)	yield (%)	M_n (g/mol)[c]	M_w/M_n[c]	f[d]
1	3	1.4	23	80	70	27 600	1.1	0.6
2	8	2	28	80	80	12 100	1.2	0.6
3	8	1	28	80	84	12 500	1.2	0.6
4	8	0.1	21.5	80	53	8 900	1.35	0.55
5[e]	4.4	1	6	100	66	22 200	1.1	0.6
6[f]	3.4	1.2	15	80	54	28 400	1.1	0.4

[a] 2-(EiB)Br: 2-bromoethyl isobutyrate; $[M]_0 = 7.5$ mol/L. [b] Molar ratios. [c] After precipitation in MeOH; calculated from GPC, using PMMA standard samples. [d] $f = M_{n,th}/M_{n,exp}$; $M_{n,th} = [M]_0/[RX]_0 \times M_{MMA} \times$ % Conv. [e] $[M]_0 = 8.3$ mol/L. [f] RX = 2-(iBP)Br, 2-bromoisobutyrophenone; $[M]_0 = 7.8$ mol/L.

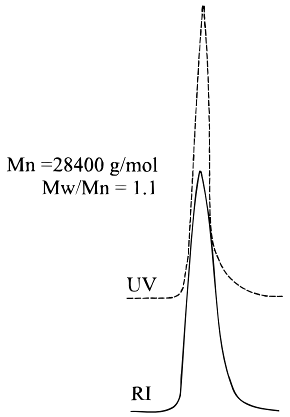

Figure 4. Comparison of SEC MWD curves of poly(MMA) obtained by UV and RI detection prepared with Ni(NCN′)Br/2-bromoisobutyrophenone (2-(iBP)Br). M_n = 28 400 g/mol; $[MMA]_0 = 7.8$ M; $[2\text{-(iBP)Br}]_0 = 34.0$ mM; $[Ni(NCN')Br]_0 = 40.8$ mM.

conversion was reached after 23 h (meaning a total conversion of 82.5% based on the total amount of added MMA). Molecular weight features (M_n = 28 800 g/mol, $M_w/M_n = 1.25$) show that a great majority of the long-lived growing species were involved in the step-growth polyaddition.

(b) Polymerization of MMA Promoted by Ni(NCN′)Br/α-Halocarbonyl Compounds. Table 2 summarizes data obtained in MMA polymerization promoted by a Ni(NCN′)Br/α-halocarbonyl (RX) system in toluene, varying different reaction parameters.

It can thus be stated that controlled polymerization occurs when activated alkyl halides are used. Suitable activated alkyl halides contain at least one α-electron-withdrawing group such as an ester, i.e, 2-bromoethyl isobutyrate (2-(EiB)Br) or a ketone, i.e, 2-bromoisobutyrophenone (2-(iBP)Br). Experimental $M_{n,exp}$ values (determined by GPC using PMMA standards) were higher than theoretically expected $\{M_{n,th} = ([M]_0/[RX]_0) \times 100 \times$ % conversion (% Conv) calculated by assuming that every α-halocarbonyl initiated one polymer chain$\}$. The initiator efficiency ($f = M_{n,th}/M_{n,exp}$) is about 0.6 and 0.4, respectively, for 2-(EiB)Br and 2-(iPB)Br. It is worthwhile pointing out that both initiator efficiencies and polydispersities were lowered during precipitation in methanol, in which oligomers were soluble.[18]

PMMA synthesized with 2-(iBP)Br and characterized by GPC showed the same average molecular weights regardless of whether UV (254 nm) or refractive index (RI) detection was used (Table 2, entry 6), while polymers prepared with 2-(EiB)Br or CCl_4 could only be detected by RI. The comparison of SEC curves as obtained by UV and RI detection (Figure 4) thus demonstrates the attachment of the phenyl ring at the α terminal end of the polymer. Moreover, both α and ω end groups of a PMMA prepared from 2-(EiB)Br were characterized by ^{1}H NMR spectroscopy. Attribution shown in Figure 5 agrees perfectly well with those reported by Sawamoto and co-workers.[10b] Characteristic resonance originating from the α-halocarbonyl moieties (2-(EiB)Br) are visible at 4.1 ppm (quartet) and 3.8 ppm (singlet). The former signal derived from the methylene protons of the ethyl ester group while the later is that of the methyl ester group adjacent to the terminal bromide at the ω-end. Excellent agreement is also found between the M_n determined by NMR and GPC (M_n = 3600 g/mol). These results confirm that α-halocarbonyl compounds are responsible for the initiation.

Interestingly enough, decreasing the molar ratio of $[Ni(NCN')Br]_0/[RX]_0$ only slightly broadened the MWD without loosing the MW control, as ascertained by the initiator efficiency values which appeared almost unaffected. Nevertheless, as evidenced by lower yields recovered after a definite reaction time, the polymerization rate decreased (entry 4 vs 2). These results

Table 3. Selected MMA Polymerization Experiments Carried Out in Toluene with Ni(NCN′)Br/2-(EiB)Br at 80 °C

entry	$[RX]_0 \times 10^2$ (mol/L)	Ni/RX[a]	$[M]_0$ (mol/L)	time (h)	yield (%)	$M_{n,th}$[b] (g/mol)	$M_{n,exp}$[c] (g/mol)	M_w/M_n
1	8	1	7.5	28	84	7 900	12 500	1.2
2	3	1.4	7.5	23	70	17 500	27 600	1.1
3	1.7	1.25	8.9	42	87	45 500	53 800	1.5
4	0.78	2.2	9.1	42	77	89 800	98 000	1.8
5	0.39	2.2	4.55	42	50	58 300	64 800	1.2

[a] Molar ratios. [b] $M_{n,th} = [M]_0/[RX]_0 \times M_{MMA} \times$ % Conv. [c] $f = M_{n,th}/M_{n,exp}$.

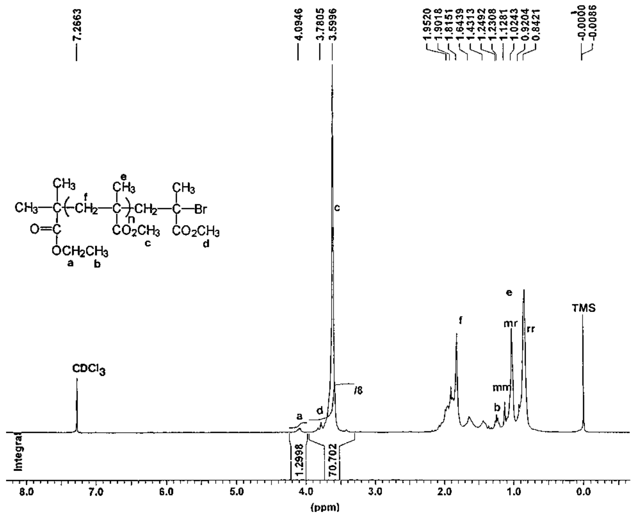

Figure 5. Representative 400 MHz ^1H NMR spectrum ($CDCl_3$, TMS) of PMMA ($M_{n,exp}$ = 3630 g/mol; M_w/M_n = 1.24).

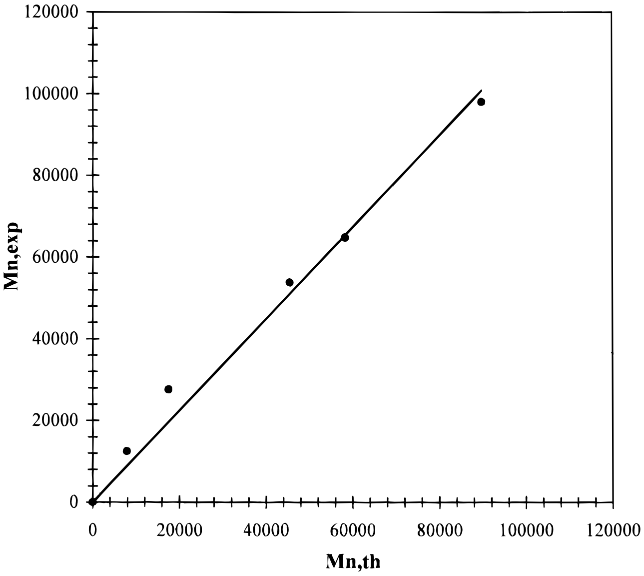

Figure 6. Dependence of $M_{n,exp}$ versus $M_{n,th}$ for selected MMA polymerizations carried out in toluene at 80 °C with Ni(NCN′)-Br/2-(EiB)Br.

probably indicate that living polymerization indeed proceeds via chain ends activation by a *catalytic* amount of arylnickel(II) complex.

Additionally, Figure 6 and Table 3 display the dependence of $M_{n,exp}$ (from GPC calibrated using PMMA standards) versus $M_{n,th}$ (obtained from $M_{n,th} = ([M]_0/[RX]_0) \times 100 \times$ % Conv) for polymerization performed at 80 °C using various $[M]_0/[2\text{-(EiB)Br}]_0$ molar ratios. Remarkably, a linear plot is observed for MW up to at least 10^5 g/mol. The slope of the straight line is 1.12, indicating a high initiator efficiency (0.89) close to unity. Some broadening of the MWD is noticed at high M_n when polymerization is carried out almost in bulk. However, dilution of the reaction medium results in a narrowing of the polydispersity as typically shown by comparing entries 4 and 5 in Table 3. Note that in the set of plots presented in Figure 6, polymers were precipitated from THF solution into methanol before GPC analysis. At low molecular weights, fractionation occurred, thus explaining the lower initiator efficiencies (f = 0.6) observed in the first two entries in Table 3.

Table 4. MMA Polymerization in Aqueous Medium (Suspension) at 80 °C with Ni(NCN′)Br/2-(EiB)Br[3]

entry	Ni/RX[b]	yield (%)	M_n[a] (g/mol)	M_w/M_n[c]	f[d]
1	0	100	>290 000	6.5	
2	1.25	98	60 000	1.7	0.4

[a] Molar ratio. [b] After precipitation in MeOH, calculated from GPC, using PMMA standard samples.

Because of the compatibility of this complex toward water, solution and/or bulk MMA polymerizations were extended to aqueous medium. The promising preliminary results obtained in aqueous “suspension”, and summarized in Table 4, indicate some control of molecular weight and unimodal molecular weight distribution (M_w/M_n = 1.7; f = 0.4). Without arylnickel(II) catalyst, only poorly controlled high molecular weight polymers difficult to solubilize in THF were obtained.

The thermal stability of PMMA is in direct relationship with the polymer structure; therefore, one could expect desirable information on the regioselectivity and the extent of termination reactions during the polymerization process. Actually, thermal degradation under nitrogen of standard radically prepared PMMA proceeds in three steps corresponding respectively to the head-to-head linkage (around 165 °C), the chain-end initiation from the vinylidene ends (around 270 °C), and the step referred to as random scission within the polymer chain (around 360 °C).[20] Thermolysis performed under nitrogen on a free radically prepared PMMA (M_n = 26 000 g/mol) and on a controlled PMMA (M_n = 28 000 g/mol) are presented in Figure 7. Thermal degradation of the polymers synthesized with Ni(NCN′)Br/2-(EiB)Br occurred around 375 °C only originating from random scission. This result is a further indication of the absence of abnormal linkages, such as the head-to-head linkages and vinylidene ends, therefore confirming the high regioselectivity and the virtual absence of termination reactions.

(c) Polymerization of n-BuMA Promoted by Ni(NCN′)Br/2-(EiB)Br. The MMA polymerization was extended to n-BuMA, a polymer which has a lower glass transition temperature than PMMA. Therefore the reaction can be performed in bulk up to high conversion at 95 °C. Figure 8 displays the conversion and the logarithmic conversion data plotted against time (% Conv vs time and $\ln[M]_0/[M]$ vs time). Kinetics is first-order in monomer and shows a constant concentration of the growing species up to high monomer conversion. It is worth pointing out that an induction period was observed. Studies to clarify this aspect are in

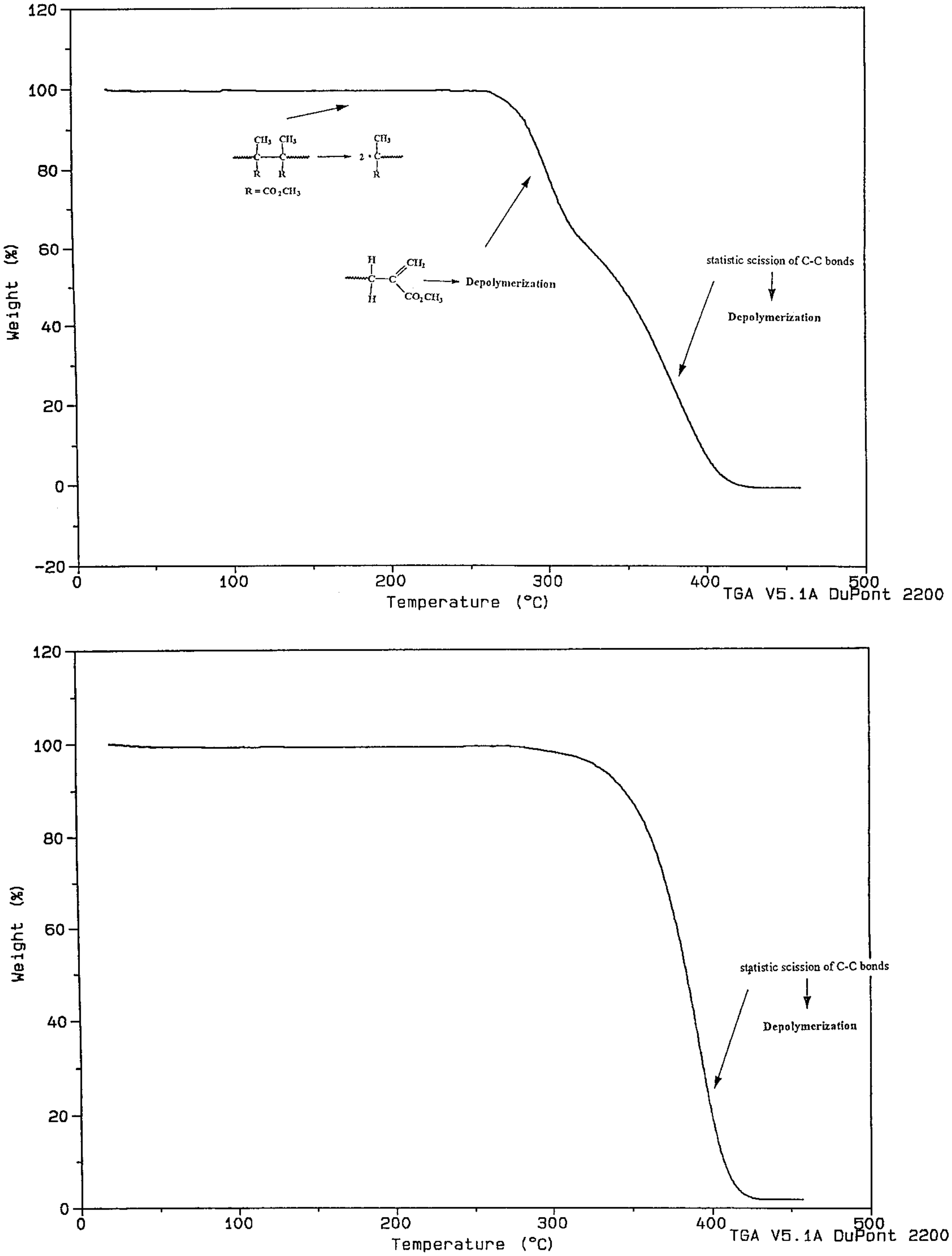

Figure 7. Comparison of TGA curves (N_2, 10 °C min^{-1}) for PMMA of comparable molecular weights and tacticity: (a) standard free radical PMMA and (b) PMMA prepared with Ni(NCN′)Br/2-(EiB)Br.

progress and will be the object of a forthcoming paper.[19] Figure 9 shows a linear dependence between the number-average molecular weights and the monomer conversion (M_n vs % Conv) while polydispersities decrease from 1.28 to 1.14. The proportional increase with conversion and the high initiator efficiency ($f > 0.8$) based on the assumption that one bromoethyl isobutyrate (2-(EiB)-Br) generates one living chain confirm our previous statement that bis(ortho-chelated) arylnickel(II) complex in the presence of activated alkyl halides initiates and controls polymerizations of methacrylic monomers.

To further demonstrate that the proposed system is living and virtually free from transfer and termination side reactions, a poly(n-BuMA-*b*-MMA) block copolymer was prepared at 80 °C (n-BuMA/MMA 50/50 v/v). n-BuMA is first polymerized quantitatively, afterwhich, a fresh MMA feed in THF (50/50 vol) is added to this unquenched polymer. The MWD remains as narrow as before the MMA addition, and the M_n of the copolymer further increases in direct proportion to the monomer conversion (Figure 10).

(d) Indications on the Polymerization Mechanism. Mechanistic investigation on the Kharasch addition[14,15] provides evidence for the participation of Ni(III) as an intermediate generated by a single electron transfer (SET) and ligand transfer oxidation. The other extreme possibility for such a polymerization pathway would be an oxidative addition/insertion/reductive elimination cycle with formation of a Ni(IV) species. However, the catalytic behavior is not in favor of a coordi-

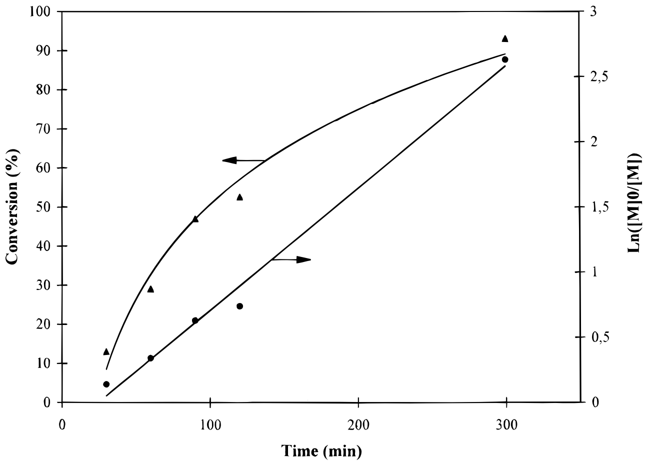

Figure 8. First-order conversion versus time plot for bulk n-BuMA polymerization at 95 °C in the presence of Ni(NCN′)-Br/2-(EiB)Br: ([2-(EiB)Br]$_0$ = 44.8 mM; [Ni(NCN′)Br]$_0$ = 51.2 mM).

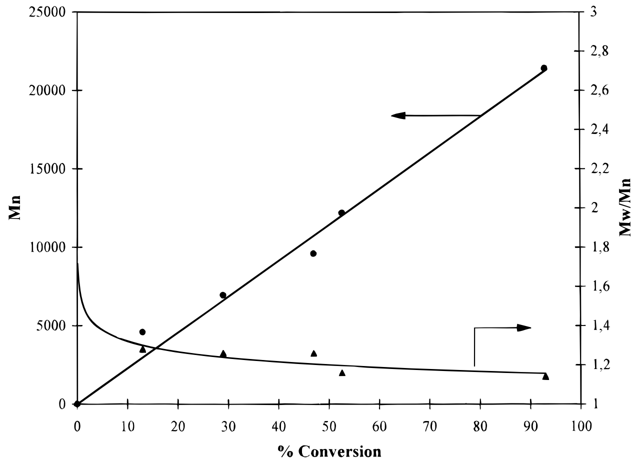

Figure 9. Dependence of the M_n and M_w/M_n with conversion for bulk n-BuMA polymerization at 95 °C in the presence of Ni(NCN′)Br/2-(EiB)Br: [2-(EiB)Br]$_0$ = 44.8 mM; [Ni(NCN′)-Br]$_0$ = 51.2 mM.

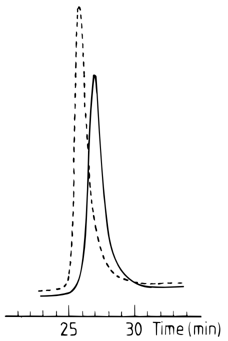

Figure 10. MWD curves of (a) poly(n-BuMA) ($M_{n,exp}$ = 11 100 g/mol, M_w/M_n = 1.18; f = 0.89) and (b) poly(n-BuMA-b-MMA) ($M_{n,exp}$ = 23 200 g/mol, M_w/M_n = 1.15) prepared with Ni(NCN′)-Br/2-(EiB)Br (molar ratio = 1.2) at 60 °C. ([2-(EiB)Br]$_0$ = 87.0 mM).

native mechanism in which the metal complex remains permanently associated with the chain end.

In order to shed more light on the polymerization mechanism, we performed the reaction at 80 °C in the presence of galvinoxyl, a well-known radical inhibitor: no polymer at all was obtained after 72 h. Furthermore, the obtained PMMA tacticity (typically rr:rm:mm = 66:31:3) is similar to the tacticity of PMMA initiated by AIBN at the same temperature. The persistence ratio (calculated from ρ = 2(m)(r)/(mr)) was found close to unity for all experiments, consistent with a Bernoullian process.

These two observations strongly support the involvement of transient radicals, maybe temporarily confined in the coordination sphere, thus considerably reducing bimolecular termination.

As already proposed by others[10,11] and supported by end groups analysis (Figures 4 and 5), we believe that the reactive alkyl halide (initiator) or the corresponding polymer chain end is reversibly activated/deactivated by a SET together with ligand transfer; nevertheless, intermediate transient species might exist involving solvent and/or alkene interaction.

But whichever the ultimate mechanism, the present results already confirm the idea that many of the Kharasch systems known in organic chemistry are convertible into polymerization initiators, if adequately adapted to the structure of the targeted monomer.

Conclusion

Our discovery that a catalytic amount of homogeneous arylnickel(II) complex mediates, with activated alkyl halides, a well-controlled or pseudoliving radical polymerization of methacrylic monomers, in organic solvents and to some extent in aqueous medium,[17] will lead us to establish the scope and mechanism of the polymerization. The possibilities to induce fine electronic tuning (functional groups in different positions of the aryl ligand) and steric modification on the bis(ortho-chelating) diamine ligand, open a large field of investigation. Work in this and other areas of polymerization using derivatives and analogues of Ni(NCN′)Br are currently in progress in our laboratory.

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