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Control of the Radical Polymerization of *tert*-Butyl Methacrylate in Water by a Novel Combination of Sodium Nitrite and Iron(II) Sulfate

C. Detrembleur,[†] Ph. Teyssié, and R. Jérôme*

Center for Education and Research on Macromolecules (CERM), University of Liège,
Sart-Tilman, B6, 4000 Liège, Belgium

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ABSTRACT: Addition of iron(II) sulfate to sodium nitrite is a new way to control the radical polymerization of *tert*-butyl methacrylate (*t*BMA) in water at 80 °C. Nitric oxide is released in the reaction medium as result of the reduction of sodium nitrite by $FeSO_4$. This reaction is of utmost importance because three repeated additions of an alkyl radical to nitric oxide leads to the formation of nitroxide radicals. The basic mechanism for the control of the radical polymerization is thus a nitroxide-mediated process.

Introduction

For a long time, anionic polymerization was the only polyaddition reaction known for livingness and, thus, for its capacity to design synthetic polymers and to tune their molecular characteristics in close relation to the envisioned application.[1] The implementation of anionic polymerization however requires drastic experimental conditions (extreme dryness, high purity of the monomer and solvent, usually low temperature, etc.), which limits large-scale production. Most polymers are commercially produced by free-radical polymerization, because of much less demanding conditions and the wide range of monomers which can be (co)polymerized. The neutrality of the radical species is however responsible for irreversible transfer and termination reactions, at the origin of uncontrolled polymerization.

Recently, the controlled radical polymerization of vinylic and (meth)acrylic monomers has been reported, which relies upon a fast exchange between growing radicals (active species) and inactive (or dormant) species. If this equilibrium is shifted enough toward the dormant species, the stationary concentration of the active species is low, which strongly limits the extent of the chain breaking reactions. At the time being, three main successful approaches have been reported. The first one, known as the nitroxyl-mediated polymerization (NMP), is based on the reversible coupling of the propagating radical with a stable free radical. This system is well suited to the (co)polymerization of styrene and derivatives.[2] It was recently extended to the polymerization of acrylates[3] and 1,3-dienes.[4] Nevertheless, the control of the polymerization of methacrylates is still a challenge. The atom transfer radical polymerization (ATRP) is the second strategy which promotes the reversible termination by the transfer of a ligand from a metal complex to the propagating radical, and vice versa. This method is effective in the polymerization of mainly (meth)acrylates and styrene derivatives.[5] The extension of this control to polymerization conducted in aqueous media[6] and particularly to emulsion polymerization must be noted for both the NMP[7] and the ATRP[8] methods. Finally, Rizzardo et al.[9] have reported on a new mechanism based on the reversible addition−fragmentation chain transfer (RAFT process). This controlled radical polymerization has the advantage to be compatible with a wide range of monomers, including monomers that contain functional groups, e.g., acid, acid salt, hydroxyl, and tertiary amine, and with aqueous media.

This paper aims at reporting on the preliminary results about the controlled radical polymerization of *tert*-butyl methacrylate (*t*BMA) in water using sodium nitrite as a mediator. The nitrite chemistry will be discussed in order to shed light on the polymerization mechanism and to account for the main experimental observations.

Experimental Section

Materials. *t*BMA from BASF was distilled just before use in order to remove the stabilizer. Bidistilled water was degassed prior to use by bubbling nitrogen for 30 min. $K_2S_2O_8$ (Aldrich), $FeSO_4 \cdot 7H_2O$ (Aldrich), AIBN (Aldrich), and $NaNO_2$ (Backer) were used as received. Liquids were transferred under nitrogen by syringes or through stainless steel capillaries.

Polymerization. a. The $NaNO_2/FeSO_4/K_2S_2O_8$ System. In a typical experiment, 0.0207 g of $NaNO_2$ (3×10^{-4} mol) and 0.0834 g of $FeSO_4 \cdot 7H_2O$ (3×10^{-4} mol) were added to the reaction flask, which was evacuated by three nitrogen−vacuum cycles. 15 mL of degassed water and 8 mL of *t*BMA (3.14×10^{-2} mol) were then added, and the flask was thermostated at 80 °C. Finally, 5 mL of a solution of 0.811 g of $K_2S_2O_8$ (3×10^{-3} mol) in 50 mL of water was added. Samples were regularly withdrawn from the polymerization medium, and the monomer conversion was calculated by ^1H NMR analysis of the organic phase. Polymerization was stopped after 24 h, thus when the medium viscosity was too high for additional samples to be picked out.

b. The $NaNO_2/FeSO_4$/AIBN System. In a typical experiment, 0.0414 g of $NaNO_2$ (6×10^{-4} mol), 0.0834 g of $FeSO_4 \cdot 7H_2O$ (3×10^{-4} mol), and 0.0492 g of AIBN (3×10^{-4} mol) were added to the reaction flask, which was evacuated by three nitrogen−vacuum cycles. 20 mL of degassed water and 8 mL of *t*BMA (5×10^{-2} mol) were then added, and the flask was thermostated at 80 °C. Samples were regularly withdrawn and analyzed as described above.

c. Synthesis and Purification of the P*t*BMA Oligomers Synthesized by the $NaNO_2/FeSO_4/K_2S_2O_8$ System and Analyzed by ESR. 0.207 g of $NaNO_2$ (3×10^{-3} mol) and 0.834 g of $FeSO_4 \cdot 7H_2O$ (3×10^{-3} mol) were added to the reaction flask, which was evacuated by three nitrogen−vacuum cycles. 75 mL of degassed water and 40 mL of *t*BMA (0,25 mol) were

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[†] Present address: Bayer AG, Leverkusen, Germany.
* To whom correspondence should be addressed.

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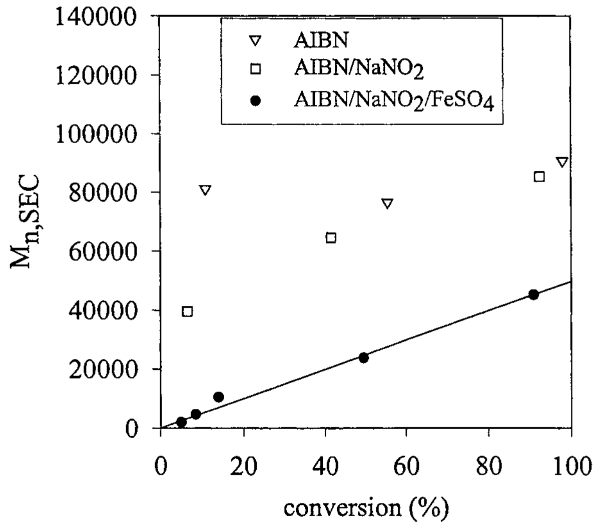


Figure 1. Dependence of $M_{n,SEC}$ on the *t*BMA conversion, in the case of initiation by AIBN in water at 80 °C in the presence or not of $NaNO_2$ and $FeSO_4$ [2 equiv of $NaNO_2$, 1 equiv of $FeSO_4$, 1 equiv of AIBN, 168 equiv of *t*BMA, water/*t*BMA = 2.5].

then added, and the flask was thermostated at 80 °C. Finally, 25 mL of a solution of 0.811 g of $K_2S_2O_8$ (3×10^{-3} mol) in 50 mL of water was added. One hour later, the monomer conversion was calculated by ^{1}H NMR analysis of the organic phase (monomer conversion: <10%), and the oligomers were extracted by 100 mL of chloroform and washed three times with water (3 × 75 mL of water) in order to remove the excess of sodium nitrite, iron(II) sulfate, and potassium persulfate. The organic phase was then dried over $MgSO_4$, filtered, concentrated under vacuum, and eluted through a silica column with chloroform. After solvent elimination under vacuum, the oligomers were dried overnight in vacuo at room temperature and analyzed by SEC and FT-IR. SEC: M_n = 1400, M_w/M_n = 1.03. IR (cm^{-1}): 2978.1, 1723.2, 1558.5, 1458.4, 1393.4, 1368.8, 1251.4, 1139.9, 847.3, 755.3.

Characterization. Size exclusion chromatography (SEC) was carried out in THF at 40 °C using a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector (columns HP PL gel 5 μm (10^5, 10^4, 10^3, and 100 Å)) and a Waters 600 liquid chromatograph equipped with a 410 refractive index detector (columns Styragel HR (HR1: 100-5000; HR2: 500-20000; HR4: 5000-600000)). The columns were calibrated with PMMA standards, and the flow rate was 1 mL/min. ^{1}H NMR spectra were recorded in $CDCl_3$ with the Bruker AM 400 and 250 MHz spectrometers at 25 °C. IR spectra were recorded with a 1720X Perkin-Elmer FT-IR spectrometer. The ESR spectra were recorded with a Bruker ESP-300 E ESR spectrometer (equipped with a temperature controller) at a frequency of 9.45 GHz, a microwave power of 20 mW, and a modulation amplitude of 1 G. The EPR tube (o.d. 4 mm) filled with 0.5 mL of solution was closed by a rubber septum. This solution was degassed three times by freeze−pump−thaw cycles, and the spectrum was recorded at the desired temperature.

Results and Discussion

It must be recalled that a previous paper from this laboratory reported on the beneficial effect of 4-methoxypyridine *N*-oxide (4-MPNO) on the radical polymerization of alkyl methacrylates.[10] Quite recently, 4-MPNO that was claimed to be 99% pure by the manufacturer was found to be contaminated by $NaNO_2$, which is actually at the origin of the control observed, as discussed hereafter.[11]

Figure 1 shows the dependence of M_n on the monomer conversion for the polymerization of *tert*-butyl methacrylate (*t*BMA) initiated by AIBN, in the presence or not of sodium nitrite and $FeSO_4$ in water at 80 °C. In absence of sodium nitrite, the polymerization is very fast (55% monomer conversion after 30 min), a high molecular weight polymer is formed at the early stage of the polymerization (Figure 1), and the polydispersity is large (Figure 2), consistent with a noncontrolled polymerization.

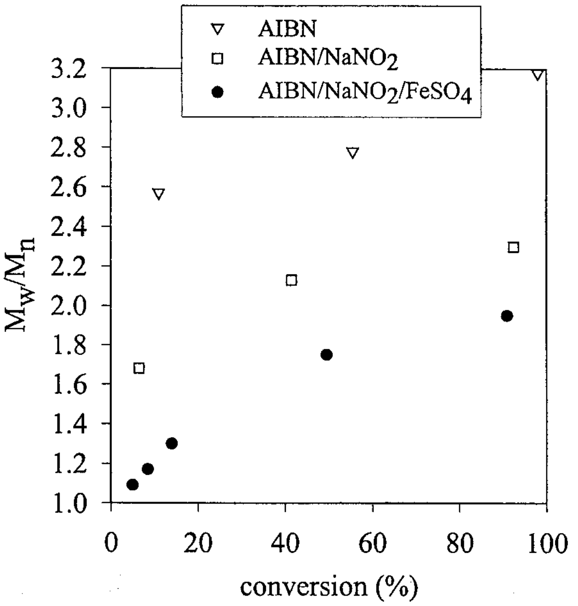


Figure 2. Dependence of the molecular weight distribution on the *t*BMA conversion, in the case of initiation by AIBN in water at 80 °C, in the presence or not of $NaNO_2$ and $FeSO_4$ [2 equiv of $NaNO_2$, 1 equiv of $FeSO_4$, 1 equiv of AIBN, 168 equiv of *t*BMA, water/*t*BMA = 2.5].

Whenever sodium nitrite is added, the polydispersity is decreased compared to the previous experiment although it remains large, and M_n increases slowly with the monomer conversion (Figures 1 and 2). The polymerization rate is still high (41% monomer conversion after 30 min), which tempers the improvement observed for the conversion dependence of M_w/M_n and M_n. The simultaneous addition of $FeSO_4$ and $NaNO_2$ to the polymerization medium results in a much lower molecular weight, all the other conditions being the same. The number-average molecular weight increases linearly with the monomer conversion, consistent with a controlled polymerization. Nevertheless, the molecular weight distribution, which is narrow at the very beginning of the polymerization (M_w/M_n < 1.1), becomes broader as the monomer conversion increases. This observation indicates that side reactions occur and limit the control of the polymerization. Furthermore, the polymerization is much slower than in the two previous cases (only 5% and 49% monomer conversion after 2 and 6 h, respectively), and an induction period of 1.5 h is observed.

Because *t*BMA is not miscible with water, it was dispersed in the aqueous phase by mechanical stirring, and no precipitation of P*t*BMA was observed during polymerization. Moreover, no sample was picked out from the polymerization medium at conversions higher than 50% because of a prohibitively high viscosity. Therefore, no experimental data are available at high monomer conversion except for the sample collected when the reaction is stopped after 24 h. This remark is valid for the experiments discussed further.

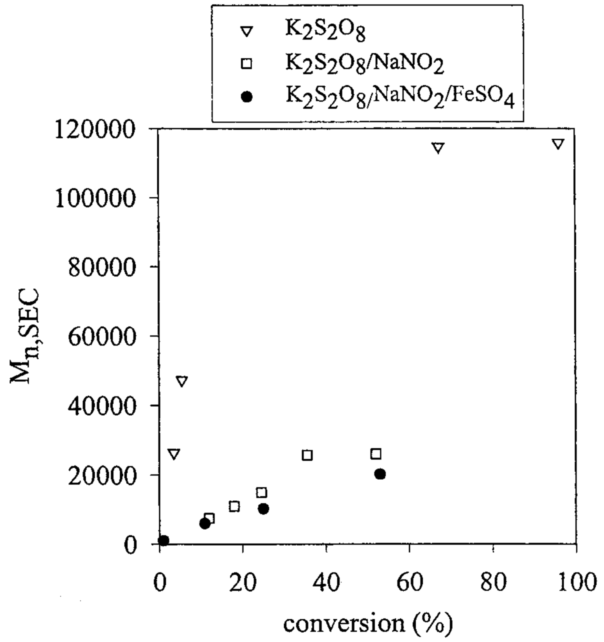


Figure 3. Dependence of $M_{n,SEC}$ on the *t*BMA conversion, in the case of initiation by $K_2S_2O_8$ in water at 80 °C, in the presence or not of $NaNO_2$ and $FeSO_4$ [2 equiv of $NaNO_2$, 1 equiv of $FeSO_4$, 1 equiv of $K_2S_2O_8$, 168 equiv of *t*BMA, water/*t*BMA = 2.5].

Because AIBN is not soluble in the aqueous phase in which sodium nitrite and $FeSO_4$ are totally soluble, potassium persulfate was used as a water-soluble initiator. Figure 3 illustrates the dependence of the number-average molecular weight on the monomer conversion for the polymerization of *t*BMA initiated by potassium persulfate in the presence or not of sodium nitrite and $FeSO_4$, in water at 80 °C.

Without sodium nitrite, the polymerization is very fast (67% monomer conversion after 45 min), and a high molecular weight polymer of a very large polydispersity ($2 < M_w/M_n < 4$; Figure 4) is rapidly formed. When sodium nitrite is added, the polymerization rate is dramatically decreased (only 55% monomer conversion after 24 h); the molecular weight of the polymer is much lower, and it increases almost linearly with the monomer conversion before it levels off at ca. 35%. Moreover, the polydispersity, which is initially low ($M_w/M_n \approx 1.1$; Figure 4), rapidly increases with the monomer conversion. All these observations are signatures of a rapid loss of control. So, the combination of $NaNO_2$ with a water-soluble initiator rather than with AIBN (without $FeSO_4$) allows the polymerization of *t*BMA to be controlled in water until 30−40% of monomer conversion. Whenever sodium nitrite is combined with $FeSO_4$, M_n linearly depends on the monomer conversion, and although it increases with the monomer conversion, the molecular weight distribution is much narrower than in absence of $FeSO_4$ (Figure 4). M_w/M_n is smaller than 1.4 at 55% monomer conversion compared to 2.35 when no iron sulfate is used. However, the polymerization slows down after a few hours, and only 55% monomer conversion is reached after 24 h.

Combination of $NaNO_2$ with potassium persulfate is thus very beneficial to the control of the radical polymerization of *t*BMA. The addition of $FeSO_4$ improves this control, although it triggers it when the polymerization is initiated by AIBN rather than by potassium persulfate.

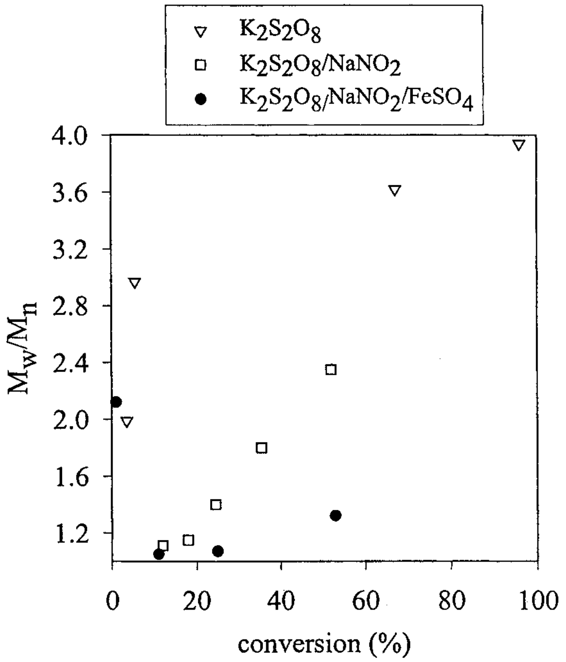


Figure 4. Dependence of the molecular weight distribution on the *t*BMA conversion, in the case of initiation by $K_2S_2O_8$, in water at 80 °C, in the presence or not of $NaNO_2$ and $FeSO_4$ [2 equiv of $NaNO_2$, 1 equiv of $FeSO_4$, 1 equiv of $K_2S_2O_8$, 168 equiv of *t*BMA, water/*t*BMA = 2.5].

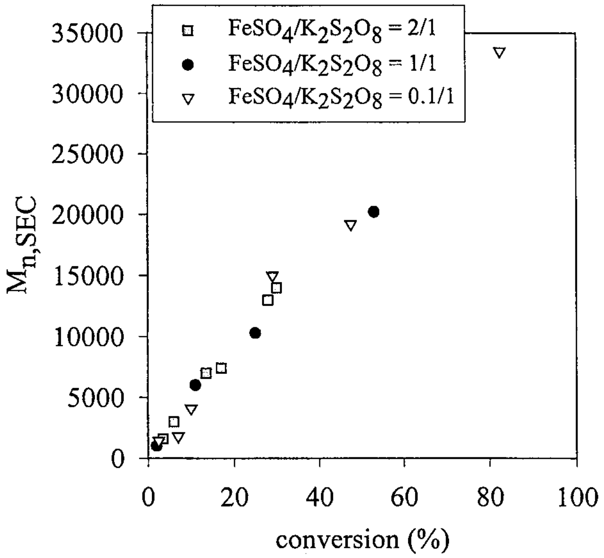


Figure 5. Dependence of $M_{n,SEC}$ on the *t*BMA conversion in water at 80 °C. The amount of $FeSO_4$ is changed, while keeping the concentration of the other components constant [2 equiv of $NaNO_2$, *x* equiv of $FeSO_4$, 1 equiv of $K_2S_2O_8$, 168 equiv of *t*BMA, water/*t*BMA = 2.5].

Influence of the Amount of $FeSO_4$. It appears that the role of iron(II) sulfate is not only to reduce $K_2S_2O_8$ with formation of a sulfate radical anion which initiates the polymerization (plus a sulfate anion)[12] but also to control the polymerization of *t*BMA initiated by potassium persulfate in the presence of sodium nitrite. To have a better insight on the role of $FeSO_4$, the amount of this salt has been changed, while keeping constant the amount of the other constituents (Figures 5 and 6).

When the $FeSO_4/K_2S_2O_8$ molar ratio is increased from 1/1 to 2/1, the same linear evolution of M_n with the monomer conversion is observed, but the polymerization

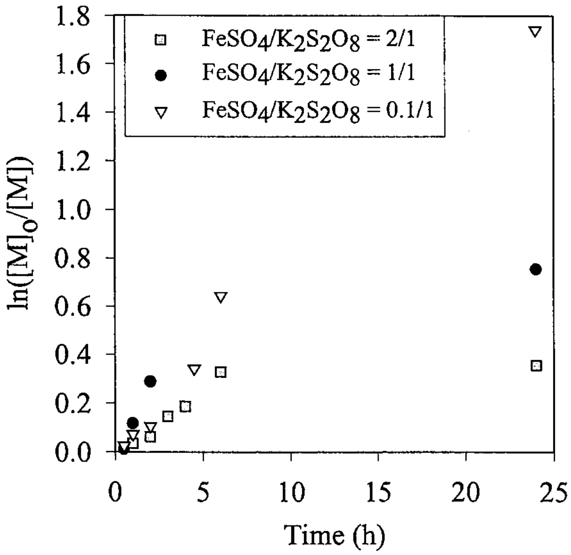


Figure 6. Time dependence of ln[M]$_0$/[M] for the polymerization of *t*BMA in water at 80 °C. The amount of $FeSO_4$ is changed, while keeping the concentration of the other components constant [2 equiv of $NaNO_2$, *x* equiv of $FeSO_4$, 1 equiv of $K_2S_2O_8$, 168 equiv of *t*BMA, water/*t*BMA = 2.5].

is slower and it stops after 24 h. Upon decreasing the $FeSO_4/K_2S_2O_8$ molar ratio from 1/1 to 0.1/1, the polymerization control is preserved as shown by the linear dependence of M_n on the monomer conversion (Figure 5) and of ln([M]$_0$/[M]) on time (Figure 6). Interestingly enough, the molecular weight is independent of the $FeSO_4/K_2S_2O_8$ molar ratio (at least in the 2/1 to 0.1/1 range), which suggests that the initiator efficiency is the same. More importantly, the monomer conversion is higher than 80% after 24 h, when the $FeSO_4/K_2S_2O_8$ molar ratio = 0.1/1 is used, compared to 55% for the $FeSO_4/K_2S_2O_8$ molar ratio of 1/1 and ca. 35% when this molar ratio is increased up to 2/1.

Although $FeSO_4$ has a beneficial effect on the control of the polymerization of *t*BMA initiated by potassium persulfate in the presence of sodium nitrite, only a small amount of this salt compared to sodium nitrite should be used to maintain the control until high monomer conversion, without however preventing the polydispersity from increasing with the monomer conversion (1.05 $\leq M_w/M_n \leq$ 2). Finally, the molecular weight of the polymer appears to depend on the amount of $K_2S_2O_8$ and not on the content of $FeSO_4$. In an additional series of experiments, the influence of the amount of $NaNO_2$ was considered.

Influence of the $NaNO_2$ Amount. The radical polymerization of *t*BMA has been studied while changing the amount of sodium nitrite at constant amount of the other constituents (Figure 7).

A linear evolution of M_n with the monomer conversion is observed at different $NaNO_2/K_2S_2O_8$ molar ratios, i.e., 2/1, 1/1, and 0.5/1. Quite interestingly, when two times more sodium nitrite is used, the molecular weight of the polymer is decreased by a factor of 2, and vice versa. Although the polymerization rate is the same at the early stage of the polymerization, the rate decreases rapidly when only a low amount of $NaNO_2$ is used ($NaNO_2/K_2S_2O_8$ = 0.5/1; Figure 8). Even though the polymerization is very slow, the molecular weight of the polymer goes on increasing with the monomer conversion.

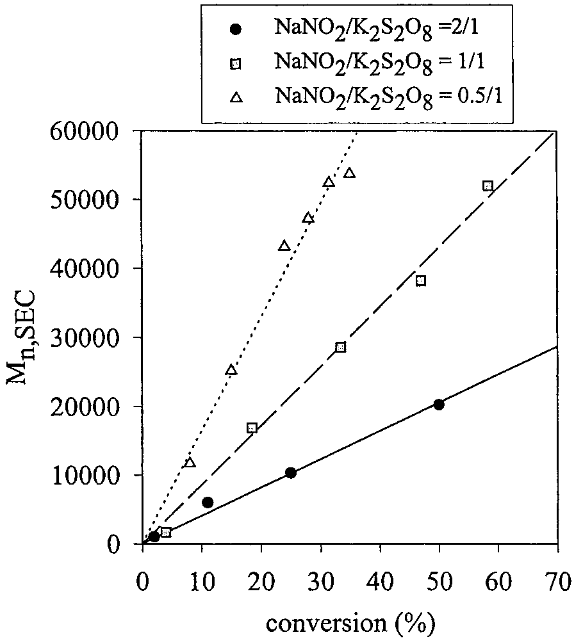


Figure 7. Dependence of $M_{n,SEC}$ on the *t*BMA conversion in water at 80 °C. The amount of $NaNO_2$ is changed, while keeping the concentration of the other components constant [*x* equiv of $NaNO_2$, 1 equiv of $FeSO_4$, 1 equiv of $K_2S_2O_8$, 168 equiv of *t*BMA, water/*t*BMA = 2.5].

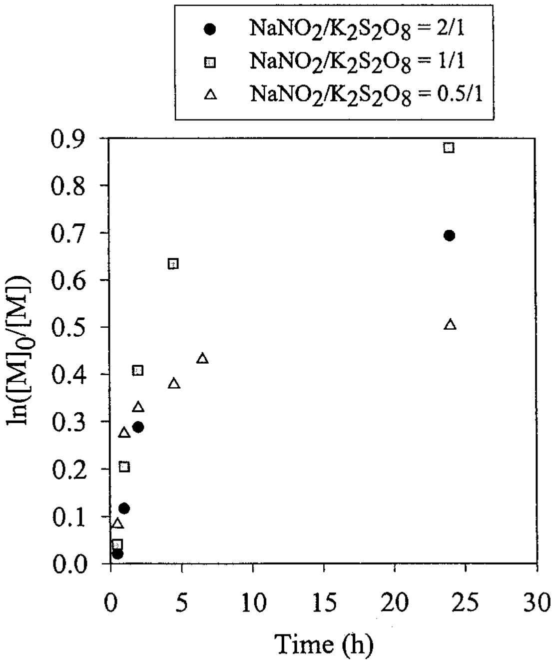


Figure 8. Time dependence of ln[M]$_0$/[M] for the polymerization of *t*BMA in water at 80 °C. The amount of $NaNO_2$ is changed, while keeping the concentration of the other components constant [*x* equiv of $NaNO_2$, 1 equiv of $FeSO_4$, 1 equiv of $K_2S_2O_8$, 168 equiv of *t*BMA, water/*t*BMA = 2.5].

Interestingly enough, the time dependence of ln[M]$_0$/[M] is not linear, indicating the slowing down of the polymerization, whereas the M_n evolution is linear with the monomer conversion. This apparent contradiction might suggest that the species responsible for the control are formed continuously during the polymerization process. Because their concentration increases in the polymerization medium with the reaction time, the active species–dormant species equilibrium is shifted

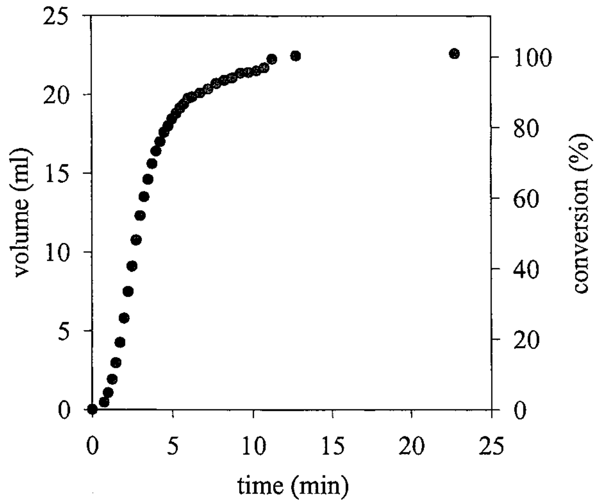


Figure 9. Volumetric measurement of NO formed by reaction of $NaNO_2$ with $FeSO_4$ in water at 80 °C [10^{-3} mol of $NaNO_2$, 10^{-3} mol of $FeSO_4$, 33.5 mL of water, 80 °C].

toward the dormant species with the polymerization progress.

So, keeping constant the amounts of monomer, potassium persulfate, and $FeSO_4$, the molecular weight of the polymer is dictated by the amount of nitrite, which should not be too low for decreasing the extent of the irreversible termination reactions.

Preliminary Approach of the Mechanism. In the scientific literature, $NaNO_2$ is a well-known inhibitor for the polymerization of water-soluble monomers at room temperature. Bortel et al.[13] speculated that the free radical polymerization of the sodium salt of acrylic acid in aqueous solution at 90 °C could be at least partly controlled by nitroxide radicals released from $NaNO_2$. This polymerization initiated by ammonium persulfate (APS) was slown down upon addition of $NaNO_2$, and M_n increased slowly with time. The polydispersity was however very large (>6.5), which indicated a very poor control of the reaction. According to Bortel et al., sodium nitrite is reversibly decomposed in aqueous media in a way which is strongly dependent on temperature and pH (eq 1).

$$2NaNO_2 + H_2O \rightleftharpoons NO + NO_2 + 2NaOH \qquad (1)$$

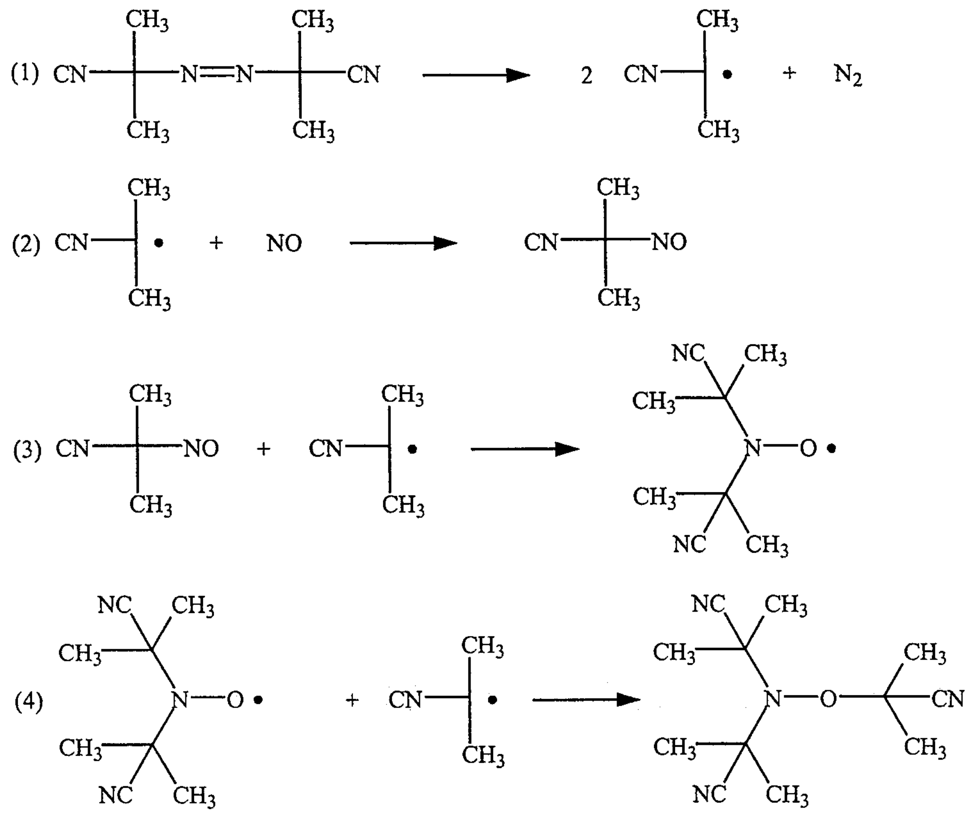
Nitric oxide has one odd electron in an antibonding π orbital, whereas nitrogen dioxide contains 17 electrons with one electron unpaired in a nitrogen or an oxygen orbital. The propagating chains can thus be trapped by these NO and NO_2 paramagnetic species, with formation of nitro compounds and nitroso compounds, respectively. The nitro compound can be further transformed into a nitroso compound by reaction with an additional radical. According to these authors, the APS radicals and the growing polymer radicals would be capped by nitroxide radicals in a dynamic equilibrium between active and dormant species, although no structure was proposed for the nitroxide radicals.

Formation of nitroso compounds by reaction of nitric oxide (NO) with free alkyl radicals has been reported independently by several authors[14,15] and formation of complexes of NO with transition-metal ions as well.[16] Moreover, the fast reduction of sodium nitrite by an acidic solution of $FeSO_4$ is known to release NO (eq 2).[17]

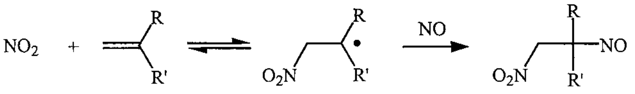
$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO \qquad (2)$$

This reaction also occurs at neutral or slightly basic pH, although much more slowly. Because the *t*BMA polymerization was carried out under the same conditions

Scheme 1



Scheme 2



as eq 2 except for the addition of sulfuric acid, the formation of NO may be postulated. To confirm this hypothesis, degassed solutions of $FeSO_4$ and $NaNO_2$ (0.03 M) were mixed and heated at 80 °C for a few minutes. An important release of NO_2 was observed when the flask was opened, as result of the direct oxidation of NO by air. Furthermore, the reaction medium became brown, in line with oxidation of iron(II) by sodium nitrite. Finally, the rate of the NO formation was measured by volumetry under the same conditions as used for the *t*BMA polymerization (same concentrations of $NaNO_2$ and $FeSO_4$). Figure 9 shows that most of NO is formed within a few minutes and that the reaction is quantitative after 15 min. Under the same conditions, but without any iron sulfate, only 4.5% of the theoretical amount of NO is formed after 30 min, and no more gas is evolved later on.

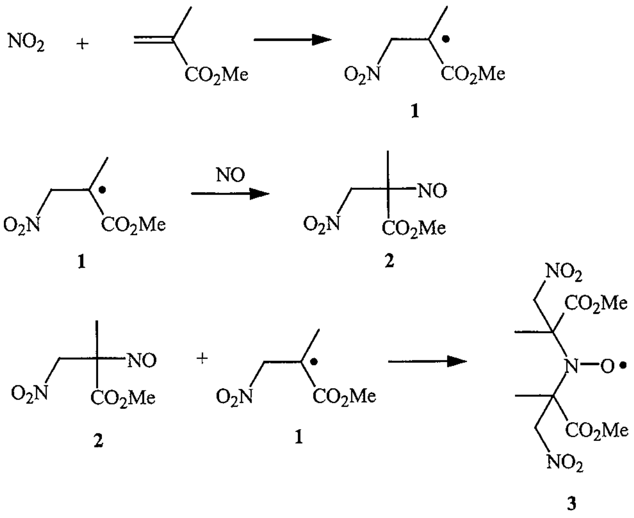
From this discussion, nitric oxide appears to be the key actor in the control of the *t*BMA radical polymerization. The main role of iron(II) sulfate would be to reduce rapidly sodium nitrite into nitric oxide which controls the polymerization. To understand better the polymerization mechanism, the chemistry of nitric oxide and related derivatives in radical reactions is discussed hereafter.

Reaction of Nitric Oxide with Free Radicals. As aforementioned, nitroso compounds are formed as result of reaction of nitric oxide with alkyl radicals.[14,18−22] These nitroso compounds are extensively used as spin-trapping agents in the study of short-lived radicals by ESR. Indeed, these radicals add to nitroso compounds and form long-lived nitroxide radicals well-suited to detection by ESR.[15,22−24] Sato and Otsu reported on the spin-trapping of a series of short-lived organic radicals by the 2-methyl-2-nitrosopropane with formation of the parent nitroxide radicals.[23] In 1953, Waters et al.[14] studied the reaction of nitric oxide with 2-cyano-2-propyl free radicals, $^{\bullet}CMe_2-CN$, released by decomposition of AIBN in boiling benzene (Scheme 1). A deep green color was first observed, which was indicative of a tertiary nitroso compound. When the reaction was complete, the product turned out to be the colorless alkoxyamine formed by the addition of three alkyl residues to the nitric oxide molecule (Scheme 1). The authors also showed that the 2-cyano-2-propyl radicals added rapidly to nitrosobenzene to form the corresponding alkoxyamine.

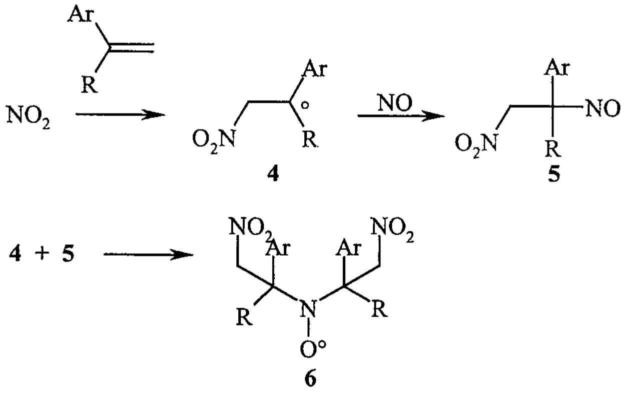
Recently, Vertommen et al.[18] and Nesvadba et al.[19] patented the synthesis of tertiary alkoxyamines by the reaction of nitric oxide with alkyl radicals and their use as initiators for the controlled radical polymerization of vinyl monomers, although the control of the polymerization remained questionable. In a more recent paper, Nesvadba successfully reported on the efficiency of new alkoxyamines, prepared by addition of free radicals to nitroso compounds, to control the polymerization of styrene.[20]

Reaction of Nitric Oxide with Functionalized Alkenes.[25,26] It is known that pure NO does not add to alkenes substituted by an acceptor or a donor group, no β-nitrosoalkyl radical being formed. However, whenever NO_2 is present, it is added to the less sterically hindered carbon of the double bond with formation of β-nitroalkyl radicals. The subsequent addition of NO to these radicals leads to α-nitroso-β-nitro compounds according to Scheme 2.

Scheme 3



Scheme 4



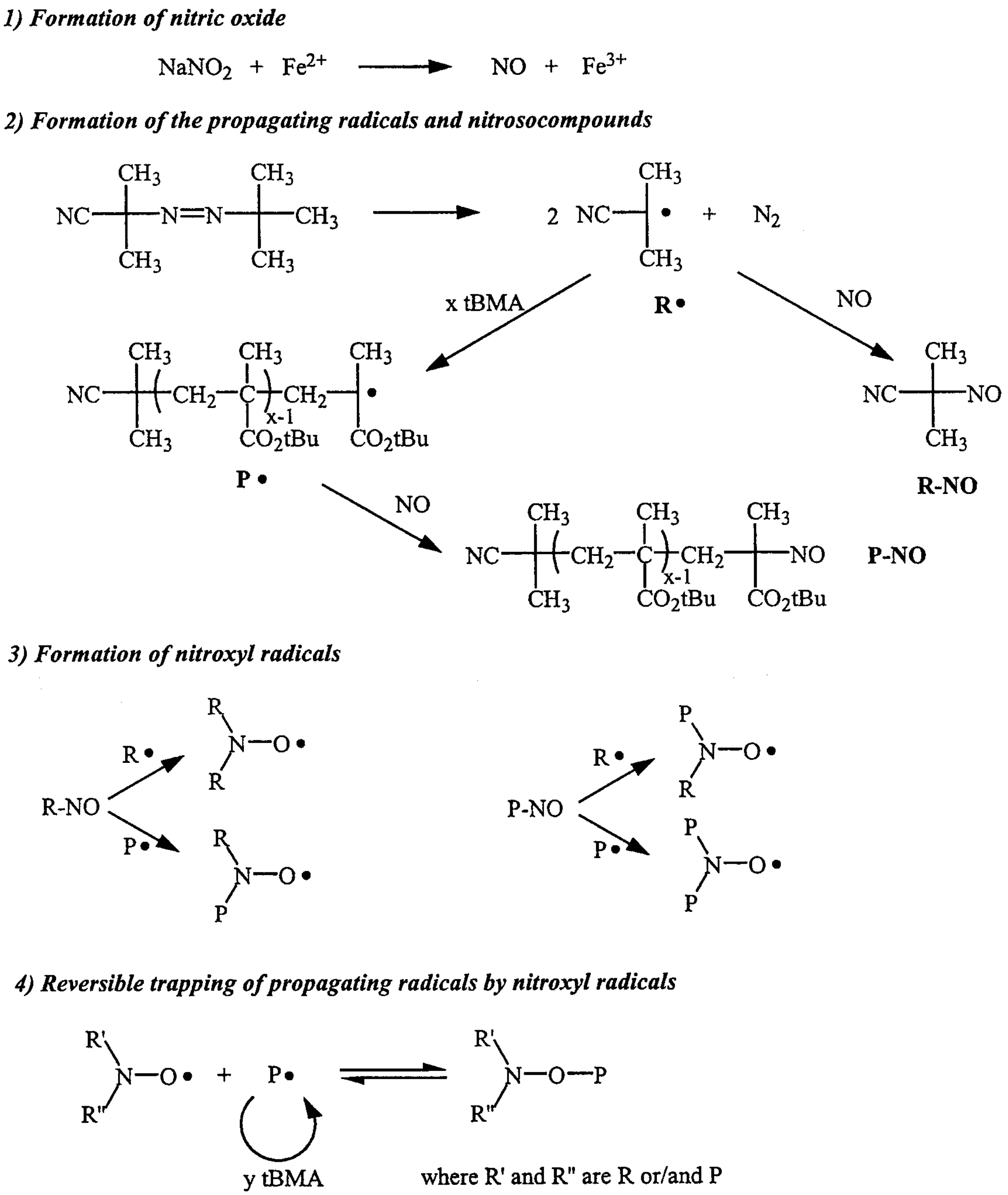
These reactions also occur with alkyl methacrylates, and Shechter et al.[27] were the first to report on the synthesis of 2-methyl-3-nitro-2-nitrosomethylpropionate ($O_2N-CH_2-C(CH_3)(CO_2Me)(NO)$; NMMA) by reaction of methyl methacrylate (MMA) with a sodium nitrite/sulfuric acid mixture (this mixture being a precursor of a NO and NO_2 mixture).

Furthermore, many authors detected a three-line ESR spectrum when MMA was reacted with NO in the presence of NO_2 at room temperature,[28] this spectrum being the signature of nitroxide radicals. Scheme 3 shows that these radicals **3** result from the addition of 2-methyl-3-nitromethylpropionate radicals **1** to methyl 2-methyl-3-nitro-2-nitrosopropionate **2**.

As shown in Scheme 4, the α-nitroso-β-nitrostyrenes **5** were formed by bubbling a NO/NO_2 mixture (1/1 molar ratio) in a styrene solution.[22] Nitroxide radicals **6** were detected, which resulted from the reaction of the β-nitro styrene radicals **4** with the α-nitroso-β-nitro styrene **5**.

Mechanism of the Controlled Radical Polymerization of *t*BMA Initiated by the $NaNO_2/FeSO_4$/Initiator System (Scheme 5). At the early stage of the polymerization, NO is formed by the rapid reduction of sodium nitrite by $FeSO_4$. The initiating radicals (2-cyano-2-propyl radicals, $R^{\bullet}$) or the propagating chains ($P^{\bullet}$) are trapped by nitric oxide and form nitroso

Scheme 5



compounds (R—NO and P—NO, respectively) as supported by the observation of a deep green-blue color. Later on, this color disappears, consistent with the addition of new radicals to the nitroso compounds and formation of nitroxide radicals. These nitroxide radicals reversibly trap the propagating radicals, thus leading to a dynamic equilibrium between dormant and active species, which is thought to be the key step for the control observed.

Three initiating/propagating radicals per NO molecule are thus needed to form the alkoxyamine which would be responsible for the control. It is difficult to estimate the amount of $NaNO_2$ and initiator required to form quantitatively the alkoxyamine because the initiator efficiency strongly depends on solvent, temperature, and dilution and because NO has a limited solubility in the liquid phase and can be lost partly when samples are picked out from the polymerization flask. Therefore, formation of the alkoxyamine may be not complete.

Moreover, formation of NO_2 by reaction of the “in situ” formed NO_2 with residual oxygen may not be precluded.[25] NO_2 can react with *t*BMA with formation of the parent β-nitroalkyl radical, which either initiates the polymerization or is trapped by NO and forms a nitroso compound and ultimately nitroxide radical (see Schemes 2 and 3).

To prove that nitrogen oxides add to *t*BMA, the gas formed by reacting equimolar solutions of sodium nitrite and iron(II) sulfate was monitored in the presence or not of *t*BMA (Figure 10). As previously reported, NO is quantitatively formed after 15 min at 80 °C. However, in the presence of *t*BMA, NO is rapidly formed at least until the release of 70% of the theoretical amount after 3.5 min. Then, the volume of gas decreases and tends to a plateau of 30—35% of the theoretical amount. So 65% of the gas (NO and NO_2) is consumed by the monomer, as qualitatively attested by the green-blue color characteristic of nitroso compounds. After 40 min

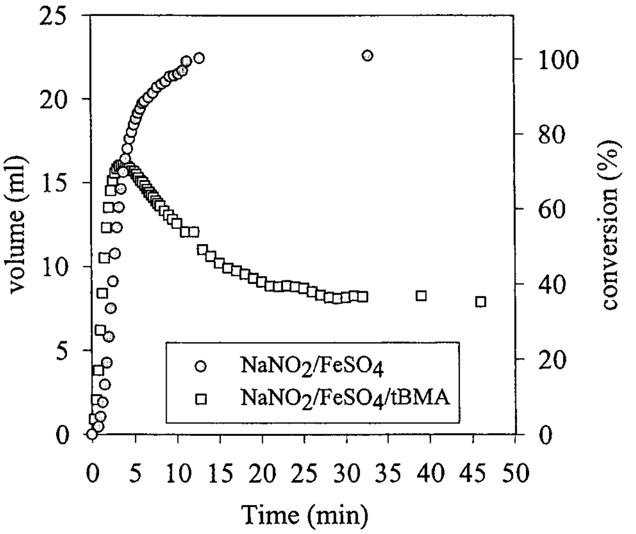
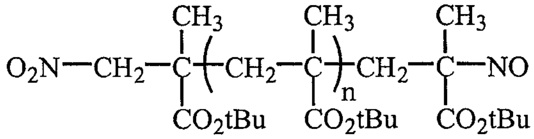


Figure 10. Volumetric measurement of NO formed by reaction of $NaNO_2$ and $FeSO_4$ in water at 80 °C, in the presence or not of *t*BMA [10^{-3} mol of $NaNO_2$, 10^{-3} mol of $FeSO_4$, 33.5 mL of water, 6.3×10^{-2} mol of *t*BMA, 80 °C].

of reaction, the organic phase was isolated and washed several times with water, and the residual monomer was eliminated under vacuum at room temperature. About 0.16 g of a yellow-brown viscous solid was collected (from 8.94 g of *t*BMA). To elucidate the structure of this residue, the IR spectrum was recorded and compared to the IR spectra of *t*BMA and poly(*t*BMA) (Figure 11). The IR spectrum of the residue does not fit *t*BMA but rather conventional poly(*t*BMA). The additional peak observed at 1561 cm^{-1} might be the signature of the NO_2 group. However, as will be reported further, nitroso compounds have a strong tendency to form dimers, which makes the assignment of the absorption peak of the NO group quite uncertain, because of its dependence on the unimer vs dimer structure.

Scheme 6



$$O_2N-CH_2-\underset{CO_2tBu}{\overset{CH_3}{C}}-\left(CH_2-\underset{CO_2tBu}{\overset{CH_3}{C}}\right)_n-CH_2-\underset{CO_2tBu}{\overset{CH_3}{C}}-NO$$

The ^1H NMR spectrum of the residue (Figure 12) confirms the similarity of structure with poly(*t*BMA), as attested by the characteristic peaks associated with poly(*t*BMA) in the 2.0−0.8 ppm range.[29] Additional peaks are observed in the 4.0−6.8 ppm range, which may be assigned to the chain ends. The singlets observed at 5.42 and 5.95 ppm are typical of the vinylidene groups (present at the chain end of some dead P*t*BMA chains), and the two multiplets at 4.2 and 4.6 ppm may be assigned to the CH_2 of the poly(*t*BMA) backbone bonded to the NO_2 group.

All these analytical data (IR, ^1H NMR, volumetric measurements) confirm the addition of nitrogen oxide to *t*BMA and formation of poly(*t*BMA) oligomers end-capped by NO_2 and more likely by NO, in agreement with the scientific literature.[25,26] Scheme 6 shows the structure of the residue which is expected to be formed by reaction of sodium nitrite and iron(II) sulfate with *t*BMA.

In addition to the nitroso compound, the parent nitroxide radical may be formed by the addition of a nitroalkyl radical as shown in Scheme 7.

Finally, to assess further the mechanism, the electron spin resonance (ESR) spectrum was recorded at 80 °C for oligomers of P*t*BMA (M_n = 1400, M_w/M_n = 1.03) synthesized by the $NaNO_2/FeSO_4/K_2S_2O_8$ system and purified before analysis (Figure 13). A triplet with A_N

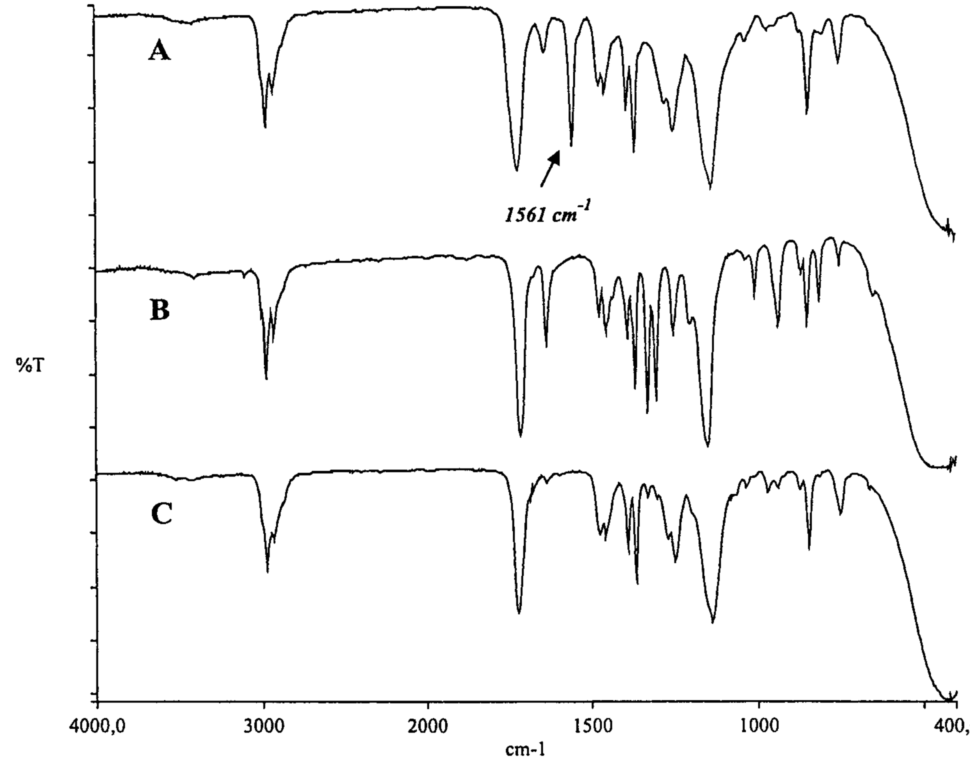


Figure 11. IR spectra of (A) the residue isolated after reaction of sodium nitrite and $FeSO_4$ with *t*BMA, (B) *t*BMA, and (C) poly(*t*BMA).

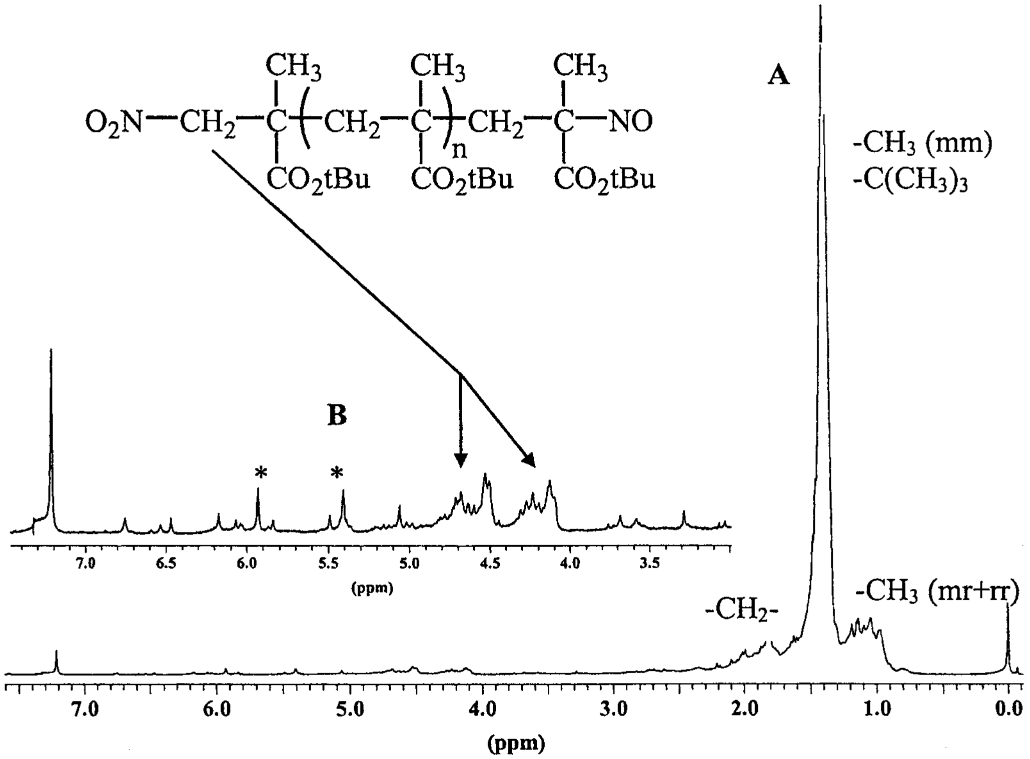
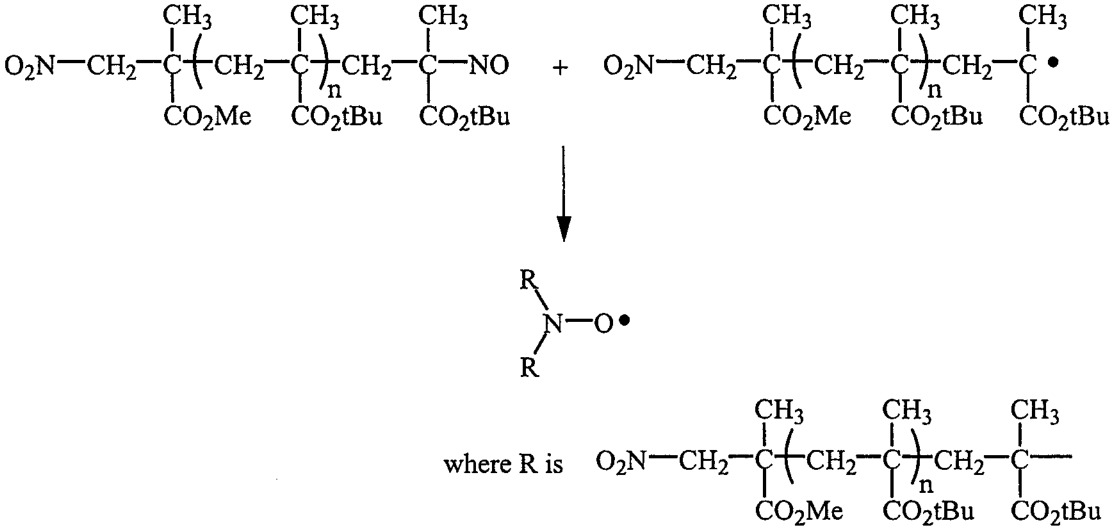


Figure 12. 400 MHz ^{1}H NMR of the reaction product of sodium nitrite with iron(II) sulfate in the presence of *t*BMA: (A) whole spectrum, (B) 3.0–7.5 ppm extended spectrum (*: vinylidene units in dead P*t*BMA chains).

Scheme 7



= 13.7 G and a *g* factor = 2.0082 are observed. This basic triplet, characteristic of nitroxide radicals,[30] confirms the formation of these species in the polymerization medium. The three-line ESR spectrum is a consequence of the hyperfine coupling to nitrogen and confirms that the nitrogen atom of the nitroxide radical is bonded to two tertiary carbons. Indeed, a more complex ESR spectrum should be observed in the case of bonding of the nitrogen atom to a secondary and/or primary carbon, as result of coupling of the radical to the hydrogen atoms bonded to these carbons. This spectrum is thus in good agreement with the structure for the nitroxide radical expected to be formed in the polymerization medium (see Scheme 5).

Consistent with the key role of NO and NO_2, the molecular weight of poly(*t*BMA) must decrease when the amount of $NaNO_2$ is increased with respect to the other reagents, in agreement with the experimental data in Figure 7. When the $NaNO_2/K_2S_2O_8$ molar ratio is 0.5/1, only one NO molecule is generated compared to four sulfate radicals. The exceeding radicals, which cannot form the alkoxyamine, are killed rapidly at the expense of the initiator efficiency. When the $NaNO_2/K_2S_2O_8$ molar ratio is increased from 1/1 to 2/1, the molecular weight decreases, although an excess of NO is formed with respect to the radicals in both the cases (on the assumption that one NO reacts with three radicals). This observation might be explained by the noncomplete dissolution of NO in the liquid phase. Moreover, more NO and NO_2 are formed when the relative amount of $NaNO_2$ is increased, such that more chains are initiated by NO_2 and their molecular weight decreases.

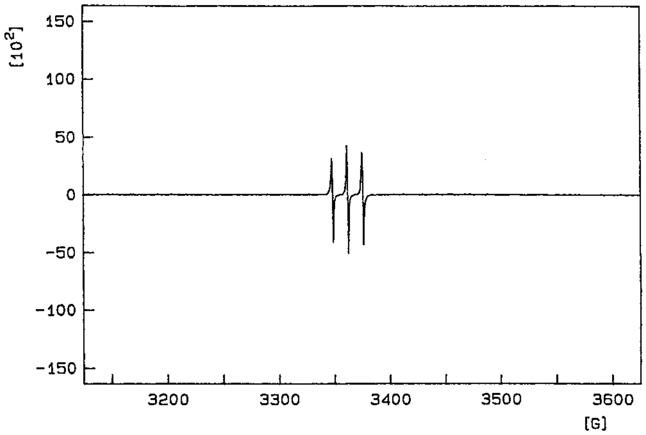


Figure 13. ESR spectrum, in toluene at 80 °C, for poly(tBMA) formed in water by the $NaNO_2/FeSO_4/K_2S_2O_8$ system [5 mg of poly(tBMA) in 0.5 mL of toluene].

Conclusions

Sodium nitrite is quite an inexpensive compound which can impart control to the radical polymerization of *t*BMA initiated by AIBN or potassium persulfate in water at 80 °C. A low amount of $FeSO_4$ is however required to observe a reasonable control, particularly when AIBN is the initiator. The molecular weight of poly(*t*BMA) is decreased when the amount of $NaNO_2$ is increased, the amount of the other constituents being kept constant.

Consistent with the scientific literature and the experiments carried out in this work, a four-step mechanism can be proposed (Scheme 5): (i) formation of nitric oxide by reduction of $NaNO_2$ by $FeSO_4$; (ii) reaction of propagating radicals with NO and formation of nitroso compounds; (iii) further reaction of propagating radicals with the nitroso compounds and formation of the parent nitroxide radicals; (iv) reversible trapping of the growing chains by the nitroxide radicals, which leads to a dynamic equilibrium between active and dormant species, at the origin of the polymerization control.

Additionally, *t*BMA can react with NO_2 formed in parallel to NO. The β-nitroalkyl radicals accordingly formed can initiate the polymerization and/or form nitroso compounds.

Although the control is imparted to the polymerization of *t*BMA by the nitrite system in water, some side reactions occur as shown by deviation of $\ln([M]_0/[M])$ vs time from linearity, and the increase in polydispersity when the monomer conversion is increased. Several causes can contribute to the gradual loss of control, i.e., the heterogeneity of the system, the number of steps leading to the dormant species with opportunity of side reactions at each step, formation of several nitroso and nitroxide compounds of a different reactivity, and the not yet optimized amounts of $NaNO_2$ and initiator. Nevertheless, this system is quite a simple method to control the radical polymerization of alkyl methacrylates in aqueous medium. It is important to note that the nitroxide-mediated polymerization (NMP) is usually known for a poor control of the polymerization of alkyl methacrylates. Therefore, the nitrite system raises new prospects in this field.

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