# Controlled Polymerization of Functional Monomers and Synthesis of Block Copolymers Using a $\beta$-Phosphonylated Nitroxide

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*Received December 27, 2002; Revised Manuscript Received February 6, 2003*

ABSTRACT: 4-Vinylpyridine (4VP) and *N*,*N*-dimethylacrylamide (DMAA) were polymerized in a controlled manner using a $\beta$-phosphonylated nitroxide (*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, commonly designated as DEPN) as a control agent. Compared to the results that had previously been reported for the nitroxide-mediated radical polymerization (NMRP) with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), the polymerization of 4VP was much faster and very well controlled up to higher monomer conversions. Unlike 4VP, the controlled radical polymerization of DMAA using different types of nitroxides had so far remained limited to a very low conversion range (typically inferior to 10%). The use of DEPN gave rise to a very significant improvement of the NMRP of DMAA by providing a good reaction control up to high conversion (approximately 60%). For the first time, the ability of DEPN to control the homopolymerization of DMAA even at high conversion allowed the synthesis of poly(DMAA-*b*-4VP) block copolymers with a hydrophilic poly(DMAA) block which was longer than the poly(4VP) block. This particular feature should fairly improve the hydrosolubility of the derived amphiphilic cationic polymers, which can be obtained by simple quaternization of the former block copolymers, and extend the scope of their applications.

## Introduction

Because of its ability to lead to macromolecules with a well-defined structure, nitroxide-mediated radical polymerization (NMRP) has now been triggering interest for almost 10 years.[1−17] Using this new type of reaction, it is possible to synthesize polymers and block copolymers with much narrower molecular weight distributions than those obtained with conventional radical polymerization and under conditions that are far more convenient than those involved in ionic polymerizations.

A lot of the pionnering works that were conducted in this field dealt with the mechanism of NMRP and, consequently, used styrene as a typical monomer for their investigations. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) was regularly chosen as a capping agent, before new nitroxides progressively appeared to allow the controlled polymerization of more monomers.[18−35] In all cases, the basic scheme of the reaction involves the thermally reversible trapping of the active polymeric chain end by a stable nitroxide radical. The high proportion of the obtained dormant chains is likely to strongly limit transfer and termination reactions, which accounts for the adjective “pseudo-living” that is sometimes improperly used to designate NMRP, as underlined by Matyjaszewski.[7]

In our laboratories, this type of polymerization has now been used for 5 years with a view to synthesizing particular block copolymers that are precursors for amphiphilic macromolecules.[36−40] Using nonconventional monomers, such as the ones that are employed in our research, systematically requires a comprehensive study of the behavior of the latter as regards NMRP. Indeed, whereas styrene and acrylate derivatives have become regularly used species, the polymerization of other monomers in the presence of nitroxides still remains uninvestigated in many cases.

We had already reported the successful polymerization of 3-vinylpyridine[37,38] and of 4-vinylpyridine[36] in the presence of TEMPO, but our results concerning the polymerization of *N*,*N*-dimethylacrylamide (DMAA) using the same nitroxide were still to be improved as regards reaction control and macromolecular polydispersity.[39] Nevertheless, a series of poly(1-hexadecyl-4-vinylpyridinium bromide-*b*-*N*,*N*-dimethylacrylamide)s had been obtained and had revealed original amphiphilic properties in aqueous medium.[40]

The synthesis of that series of block copolymers had required the preparation and characterization of a poly(4-vinylpyridine) first block whose polydispersity was low, followed by the chain extension of that macroinitiator using DMAA as a comonomer. Although TEMPO provided very satisfactory results with 4-vinylpyridine, the major problem at that time was the poor control of the polymerization of *N*,*N*-dimethylacrylamide allowed by TEMPO at high conversion.[39] Therefore, the synthesis of block copolymers presenting a poly(DMAA) second block with a wide length range from a TEMPO-terminated poly(4VP) macroinitiator was seriously impeded when DMAA was used as the comonomer. Consequently, in the previous series of amphiphilic macromolecules, the proportion of DMAA units could not exceed 40 mol %.

Yet, there was no doubt that block copolymers with a high proportion of hydrophilic DMAA units would certainly lead to a much improved solubility of the derived amphiphilic polymers in aqueous medium and, thus, enable to overcome one of the limitations of the amphiphilic block copolymers of the former series for potential applications.

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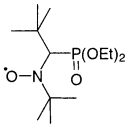
10.1021/ma0260086 CCC: $25.00

**Scheme 1. *N-tert*-Butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) Nitroxide, Commonly Designated as DEPN**



Aiming at synthesizing the same type of macromolecules but, this time, with a higher proportion of DMAA units, we reversed the order of the steps involved in the synthetic pathway. Thus, in the new synthesis scheme, DMAA was homopolymerized first. The nitroxide-terminated poly(DMAA) was then used as a macroinitiator and chain-extended with 4VP, as the polymerization of 4VP was much easier to control than that of DMAA. The first step obviously required a nitroxide radical which was likely to control the polymerization of DMAA up to high conversion values much better than TEMPO. Considering the progress that had been triggered in the field of NMRP by the introduction of $\beta$-phosphonylated nitroxides,[20−24,26−31] *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (DEPN) was chosen as a control agent.

We report here on the behavior of two functional monomers, i.e., 4VP and DMAA, as regards their homopolymerization in the presence of either DEPN or a derived alkoxyamine in comparison with TEMPO. On the basis of the homopolymerization results, the synthesis of the targeted diblock copolymers is then described.

## Experimental Section

**Synthesis of *N-tert*-Butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) Nitroxide (DEPN).** DEPN was obtained by oxidation of 2,2-dimethyl-1-(1,1-dimethylethylamino)propyldiethylphosphonate with oxone, the synthesis being adapted from refs 27, 29, and 30. The obtained crude oil was purified by chromatography on silica (eluent: chloroform/isopropyl ether, 91/9, v/v). A very careful fractionation led to DEPN (yield: 40%) with a purity higher than 95% as confirmed by reverse-phase HPLC analysis (Figure 1) (Chromolith RP18e Merck column (100 × 4.6 mm); eluent: 30/70, v/v acetonitrile/water mixture; flow rate: 2 mL min$^{-1}$; Shimadzu UV detector: detection at 210 nm).

**Preparation of the DEPN-Based Alkoxyamine *N*-Tertiobutyl-*N*,1-diethylphosphono-2,2-dimethylpropyl-*O*,1-phenylethylhydroxyamine (Sty-DEPN).** The synthesis of Sty-DEPN was adapted from refs 22 and 28−30. Copper, copper bromide, pentamethyldiethylenetriamine (PMDETA), and (1-bromoethyl)benzene (Aldrich) were used as received. Dichloromethane was distilled on phosphorus pentoxide and stored on molecular sieves.

In a three-necked round-bottom flask, under a nitrogen atmosphere, 2.05 g (11 mmol) of (1-bromoethyl)benzene dissolved in 50 mL of dichloromethane was added to a mixture of 3.46 g (20 mmol) of PMDETA, 1.14 g (8 mmol) of copper bromide, 0.51 g (8 mmol) of copper, 2.94 g of crude DEPN, and 50 mL of dichloromethane. The mixture was left to react for 4 days under vigorous stirring and a nitrogen atmosphere at room temperature. The solid residue was eliminated by filtration, and the organic phase was washed with distilled water until it became limpid. The latter was then dried on magnesium sulfate, and dichloromethane was removed by evaporation under reduced pressure at room temperature. The alkoxyamine was purified by chromatography on silica (eluent: hexane/diethyl ether, 4/1, v/v). A colorless oil (1.92 g, yield 48%) was obtained as a mixture of two diastereoisomers. Given the original purity of crude DEPN, the reaction could be considered quantitative. $^{1}$H NMR and $^{13}$C NMR chemical shifts and spin coupling constants obtained for the mixture of the two diastereoisomers were fully consistent with their chemical structures. The composition (62/38%) of the diastereoisomer mixture was determined by $^{31}$P NMR. NMR spectra were recorded using a Bruker DRX 400 spectrometer.

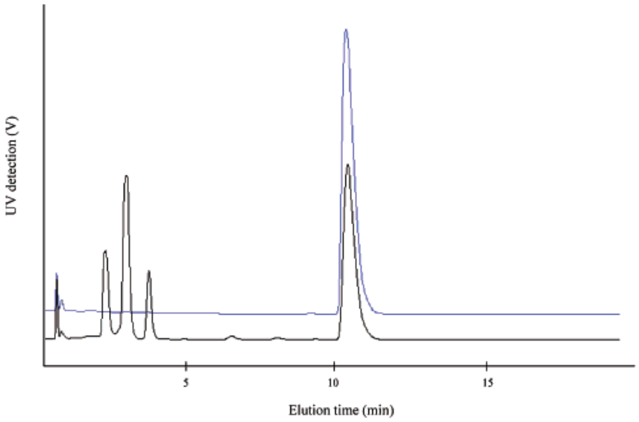


**Figure 1.** Reverse-phase high-pressure liquid chromatograms of crude (below) and purified (above) DEPN. Eluent: acetonitrile/water (30/70, v/v); flow rate: 2 mL min$^{-1}$; detection wavelength: 210 nm.

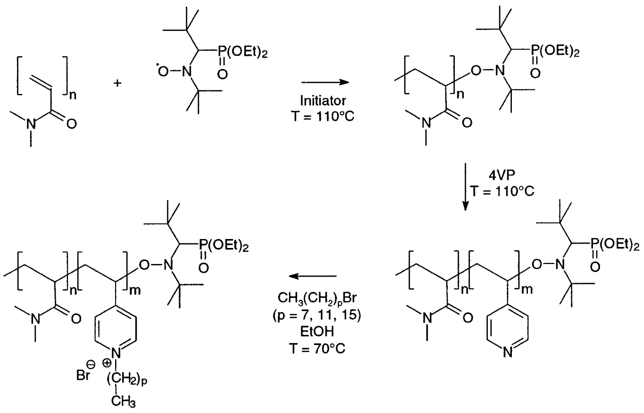
$^{1}$H NMR (400 MHz, CDCl$_3$): First diastereoisomer: $\delta$ (ppm) = 0.88 (t, 3H, $J_{\mathrm{H-H}}$ = 7.2 Hz), 1.21 (s, 18H), 1.23 (t, 3H, $J_{\mathrm{H-H}}$ = 7.3 Hz), 1.56 (d, 3H, $J_{\mathrm{H-H}}$ = 6.5 Hz), 3.40 (d, 1H, $J_{\mathrm{H-p}}$ = 26.1 Hz), 3.20−4.20 (m, 4H), 5.24 (q, 1H, $J_{\mathrm{H-H}}$ = 6.5 Hz), 7.2−7.5 (m, 5H). Second diastereoisomer: $\delta$ (ppm) = 0.84 (s, 9H), 1.25 (s, 9H), 1.32 (t, 3H, $J_{\mathrm{H-H}}$ = 7.1 Hz), 1.35 (t, 3H, $J_{\mathrm{H-H}}$ = 7.0 Hz), 1.60 (d, 3H, $J_{\mathrm{H-H}}$ = 6.7 Hz), 3.35 (d, 1H, $J_{\mathrm{H-P}}$ = 26.1 Hz), 3.90−4.50 (m, 4H), 5.00 (q, 1H, $J_{\mathrm{H-H}}$ = 6.5 Hz), 7.10−7.40 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$): First diastereoisomer: $\delta$ (ppm) = 16.45 (2d, $J_{\mathrm{C-P}}$ = 7.2 Hz), 21.45 (s), 28.47 (s), 30.92 (d, $J_{\mathrm{C-P}}$ = 5.5 Hz), 35.61 (d, $J_{\mathrm{C-P}}$ = 6.0 Hz), 58.85 (d, 7.5 Hz), 61.83 (d, $J_{\mathrm{C-P}}$ = 7.0 Hz), 70.25 (d, $J_{\mathrm{C-P}}$ = 138.8 Hz), 78.63 (s), 127.63 (s), 128.12 (s), 128.16 (s), 143.57 (s). Second diastereoisomer: $\delta$ (ppm) = 16.53 (d, $J_{\mathrm{C-P}}$ = 7.3 Hz), 17.02 (d, $J_{\mathrm{C-P}}$ = 5.2 Hz), 24.34 (s), 28.78 (s), 30.38 (d, $J_{\mathrm{C-P}}$ = 5.7 Hz), 35.88 (d, $J_{\mathrm{C-P}}$ = 6.0 Hz), 59.08 (d, $J_{\mathrm{C-P}}$ = 7.5 Hz), 61.43 (d, $J_{\mathrm{C-P}}$ = 6.5 Hz), 70.17 (d, $J_{\mathrm{C-P}}$ = 138.6 Hz), 85.61 (s), 127.24 (s), 127.38 (s), 128.24 (s), 145.71 (s). $^{31}$P NMR (162 MHz, CDCl$_3$): First diastereoisomer: $\delta$ (ppm) = 24.1, second diastereoisomer: $\delta$ (ppm) = 25.3.

**Polymerizations.** Commercial 4VP and DMAA (Aldrich) were distilled under reduced pressure (40 and 65 °C/1 mmHg, respectively). 2,2′-Azobis(2-methylpropionitrile) (AIBN, Acros Organics) was recrystallized from methanol and dried under vacuum at room temperature.

Typically, monomer, initiator, and nitroxide were introduced in a Schlenk-type reactor. The mixture was degassed by several freeze−thaw cycles and finally purged with argon. The vessel was then immersed in a preheated oil bath (110 °C). Magnetic stirring and temperature control (±1 °C) were imposed throughout the reaction. The reaction was stopped by cooling the flask after different polymerization times. Excess monomer was evaporated under reduced pressure (0.5 mmHg), and the polymer was recovered as a powder after careful drying in a vacuum oven (0.5 mmHg) at 60 °C for 48 h. Conversion was determined by weighing the obtained products. For the bulk polymerization of 4VP with a bicomponent AIBN/DEPN system, the reactor was originally charged with 4 mL of 4VP, 6.6 mg ($4.02 \times 10^{-5}$ mol) of AIBN, and 21.2 mg ($7.21 \times 10^{-5}$ mol) of DEPN. In the case of the bulk polymerization of 4VP using the Sty-DEPN alkoxyamine as an initiator, 16.0 mg ($4.01 \times 10^{-5}$ mol) of alkoxyamine and 4 mL of 4VP were introduced in the reactor. As regards the bulk polymerization of DMAA with the AIBN/DEPN system, 4 mL of DMAA was added to 14.4 mg ($8.78 \times 10^{-5}$ mol) of AIBN and 51.7 mg ($1.76 \times 10^{-4}$ mol) of DEPN. In the case of the bulk polymerization of DMAA with Sty-DEPN alkoxyamine

**Scheme 2. Synthetic Pathway To Obtain Poly(DMAA-*b*-4VP) Amphiphilic Block Copolymers**



in the presence of an excess DEPN, 4 mL of DMAA was used along with 35.1 mg ($8.80 \times 10^{-5}$ mol) of Sty-DEPN and 17.1 mg ($5.82 \times 10^{-5}$ mol) of DEPN.

The copolymerization procedure was the same as the one used for homopolymerizations. As for the original amounts, 2 g ($7.87 \times 10^{-5}$ mol) of DEPN-terminated poly(DMAA) used as a macroinitiator was added to 9.3 mL of 4VP. The features of the macroinitiator were as follows: $M_n = 25\,400$ g mol$^{-1}$; $M_w/M_n = 1.23$.

**Molecular Weight Determination.** The average molar weights of the polymers were determined by size exclusion chromatography (SEC). Prior to any experiment, the polymers were left to dissolve overnight in *N*,*N*-dimethylformamide (Aldrich, HPLC grade, 99.9+%), which was also used as an eluent (elution rate: 1 mL min$^{-1}$). Before injection, the solutions were filtered through PTFE membranes (Alltech, average pore diameter: 200 nm). The temperature was maintained at 40 °C during all SEC experiments. Measurements were performed on a Waters device equipped with a Styragel HR4 ($7.8 \times 300$ mm) column ($10^3$–$5 \times 10^6$ g/mol). The system had previously been calibrated with poly(2-vinylpyridine) standards (Fluka) and also with polystyrene standards (Altergen, Schiltigheim, France) as a comparison. Sample detection was performed using a Waters 410 differential refractometer. The chromatograms were then processed with the Millenium software.

## Results and Discussion

As we aimed at preparing block copolymers with both 4VP and DMAA units, our first objective consisted in making sure that DEPN was able to control the homopolymerization of each of these monomers.

Two different systems were investigated for each monomer, i.e., a bimolecular one (system I), in which the polymerization was carried out in the presence of DEPN along with AIBN as an initiator, and a monomolecular one (system II), in which an alkoxyamine derived from DEPN was the only species to both initiate and control the reaction.

Whatever the used system and monomer, DEPN enabled to control the homopolymerization of 4VP and DMAA with polymerization rates that were much higher than those observed with TEMPO. Contrary to 4VP, DMAA had never been polymerized in a controlled manner by NMRP up to high conversion so far. Compared to former nitroxides that had been reported for the NMRP of DMAA,[25,39,41] DEPN clearly provided a breakthrough for the polymerization of this particular monomer by extending the range of monomer conversion for which the polymerization was controlled from 10% to almost 60%.

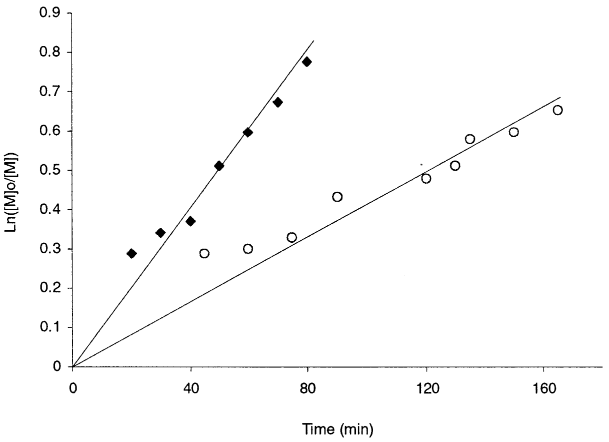


**Figure 2.** Bulk polymerization of 4VP at 110 °C; ln([M]$_0$/[M]) vs time. System I (○): [AIBN]$_0$ = $10^{-2}$ mol L$^{-1}$; [DEPN]$_0$/[AIBN]$_0$ = 1.8. System II (◆): [alkoxyamine]$_0$ = $10^{-2}$ mol L$^{-1}$.

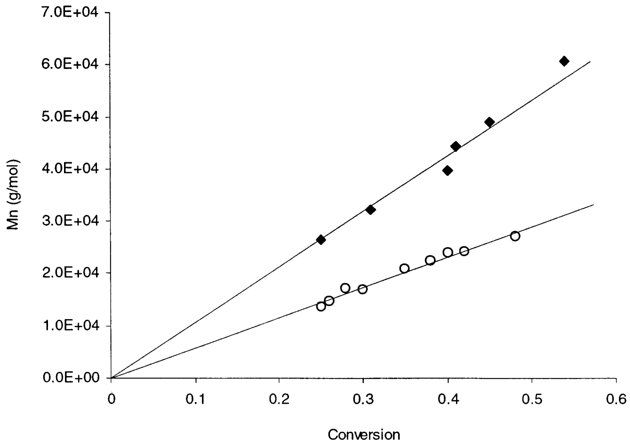


**Figure 3.** Bulk polymerization of 4VP at 110 °C; $M_n$ vs conversion. System I (○): [AIBN]$_0$ = $10^{-2}$ mol L$^{-1}$; [DEPN]$_0$/[AIBN]$_0$ = 1.8. System II (◆): [alkoxyamine]$_0$ = $10^{-2}$ mol L$^{-1}$.

These very promising results represented a first step toward the synthesis of poly(DMAA-*b*-4VP) new block copolymers which would combine significant molecular weights for both blocks (up to $M_n = 20\,000$ g mol$^{-1}$) with a wide composition range.

**Homopolymerization of 4-Vinylpyridine.** It is commonly admitted that a nitroxide-mediated polymerization can be considered controlled as soon as the number of propagating free polymeric radicals is constant and, at the same time, the molar weight of the obtained macromolecules is proportional to monomer conversion.[7,10] In the case of 4VP, Figures 2 and 3 gather the results obtained for the plots of both ln([M]$_0$/[M]) vs time and $M_n$ vs conversion, where [M]$_0$, [M], and $M_n$ respectively stand for monomer original and current concentration in the bulk and polymer number-average molar weight. It must here be reminded that a linear plot of ln([M]$_0$/[M]) as a function of time guarantees a constant number of propagating polymeric radicals, as shown by integration of eq 1 which describes monomer consumption:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{R}^\bullet][\mathrm{M}] \qquad (1)$$

where $k_p$ and [R$^\bullet$] respectively stand for the propagation rate constant of the polymerization and the concentration in propagating polymeric radicals in the bulk.

For the bimolecular system (system I) as well as for the monomolecular system (system II), the two graphic

**Table 1. Bulk Polymerization of 4VP at 110 °C Using System I; [AIBN]$_0$ = $10^{-2}$ mol L$^{-1}$; [DEPN]$_0$/[AIBN]$_0$ = 1.8**

| conv | theor $M_n$ ($10^3$ g/mol) | $M_n$ ($10^3$ g/mol) (poly(2VP) standards) | $M_w/M_n$ (poly(2VP) standards) |
|---|---|---|---|
| 0.25 | 12.2,[a] 13.4[b] | 13.6 | 1.12 |
| 0.26 | 12.7,[a] 14.2[b] | 14.9 | 1.12 |
| 0.28 | 13.7,[a] 15.4[b] | 17.2 | 1.10 |
| 0.30 | 14.6,[a] 16.2[b] | 17.1 | 1.11 |
| 0.35 | 17.0,[a] 18.7[b] | 20.9 | 1.11 |
| 0.38 | 19.0,[a] 20.7[b] | 22.5 | 1.09 |
| 0.40 | 19.8,[a] 21.8[b] | 24.0 | 1.13 |
| 0.42 | 20.6,[a] 23.0[b] | 24.2 | 1.20 |
| 0.48 | 23.0,[a] 26.0[b] | 27.1 | 1.21 |

[a] Considering the original AIBN concentration as determining. [b] Considering the original DEPN concentration as determining.

criteria required to ascertain a controlled polymerization were fulfilled, as proved by the corresponding plots (Figures 2 and 3). As concerns the kinetic plot (Figure 2), a positive shift at the very beginning of the polymerization was observed with the bimolecular system, which seems to indicate a slightly poorer reaction control early on, corresponding to a possible higher radical concentration. However, Figure 3 confirms the control of the number of growing chains throughout the polymerization.

Compared to the former results[36] obtained with TEMPO for 4VP, the reaction was much faster with DEPN even at a much lower temperature (i.e., 110 and 138 °C for DEPN and TEMPO, respectively). The increase in polymerization rate with the acyclic nitroxide DEPN was expected from the faster rate of homolysis of the dormant species obtained by coupling with acyclic rather than cyclic nitroxides, as shown for instance by Marque et al.[42] and Kazmaier et al.[4] When a bimolecular system DEPN/AIBN was used, the polymerization was also very well controlled (Figures 2 and 3). It must be emphasized that the polymerization control was well achieved for a [DEPN]$_0$/[AIBN]$_0$ ratio which was equal to 1.8 (i.e., inferior to 2).

Table 1 deals with the homopolymerization of 4VP in the presence of the bimolecular system DEPN/AIBN (system I) and compares the experimental values of the number-average molar weights of the obtained polymers with theoretical values worked out when considering either the initiator (AIBN) or the capping agent (DEPN) as the species whose original concentration determines the number of chains. According to the results gathered in Table 1, it seems that DEPN is responsible for the actual number of macromolecules and, consequently, their molar weights. In good agreement with former polymerization data obtained with DEPN in different systems,[23,27,31,43] the experimental molecular weights were usually slightly higher than the theoretical ones. An initiator efficiency inferior to 1 might account for the difference between theoretical and experimental molar weights for system I and would also account for the low amount of DEPN which was nevertheless sufficient to control the polymerization in the bimolecular system. An irreversible decomposition of DEPN throughout the polymerization, which has been reported to occur at elevated temperatures,[43] would also produce the same effects on molecular weights.

Thermal polymerization, which is sometimes mentioned as a key phenomenon in NMRP, does not seem to occur in a significant way although its contribution is certainly difficult to assess because thermal polymerization and a lowered efficiency of the initiator would have antagonistic effects on molecular weights. Hence, both effects would have a tendency to compensate.

**Table 2. Bulk Polymerization of 4VP at 110 °C Using System II; [Alkoxyamine]$_0$ = $10^{-2}$ mol L$^{-1}$**

| conv | theor $M_n$ ($10^3$ g/mol) | $M_n$ ($10^3$ g/mol) (poly(2VP) standards) | $M_w/M_n$ (poly(2VP) standards) |
|---|---|---|---|
| 0.25 | 24.6 | 26.5 | 1.36 |
| 0.31 | 30.6 | 32.2 | 1.28 |
| 0.40 | 38.7 | 39.7 | 1.27 |
| 0.45 | 44.1 | 49.0 | 1.22 |
| 0.49 | 47.4 | 47.5 | 1.31 |
| 0.54 | 52.0 | 60.6 | 1.15 |

However, all these results obviously need considering while keeping in mind that the poly(2VP) standards used to characterize the samples by SEC do not exactly correspond to poly(4VP) macromolecules (even though they are very closely related), which induces an incertitude as regards molar weight characterization.

As shown in Table 2, when homopolymerized in the presence of system II, 4VP yields molar weights which are really close to the theoretical expectations. (In this case, the [DEPN]$_0$/[initiator]$_0$ ratio is equal to 1 as the same molecule plays the role of both the initiator and the capping agent.) Nevertheless, the polydispersity indices turned to be a little higher than those obtained with system I. Moreover, the kinetic comparison between systems I and II (Figure 2) shows that the polymerization rate is twice as low with a bimolecular system as it is with an alkoxyamine. Both of the former observations are unusual so far but might be interpreted again by considering an initiator efficiency that is inferior to 1 for the bimolecular system. In that case, the excess of nitroxide with respect to the active initiating radicals would be responsible for a much slower kinetics and a stronger homogeneity of the molecular weight distribution, which is in very good agreement with former observations made on the systems styrene/DEPN and *n*-butyl acrylate/DEPN systems.[17,23,27,31,43]

**Homopolymerization of *N,N*-Dimethylacrylamide.** Contrary to 4VP, DMAA had never been polymerized in a controlled manner up to high conversions so far. Systems I and II were used here as well. As already observed during our former investigations with TEMPO,[36] the NMRP of DMAA is much slower than that of 4VP. With the bimolecular system (system I), an original AIBN initial concentration equal to $10^{-2}$ mol L$^{-1}$ along with a [DEPN]$_0$/[AIBN]$_0$ ratio of 1.8 (the latter conditions corresponding to those encountered while working on 4VP) was not sufficient to guarantee a controlled reaction. It can be supposed that, with too little AIBN, chemical initiation becomes overcome by thermal radical generation, which prevents satisfactory control. Our experiments were then conducted with an initial AIBN concentration in the bulk which was equal to $2.2 \times 10^{-2}$ mol L$^{-1}$ and a [DEPN]$_0$/[AIBN]$_0$ ratio equal to 2. These conditions enabled a good control of the radical polymerization of DMAA up to high conversion (almost 60%) (Figures 4 and 5, Table 3). Accordingly, the alkoxyamine only controlled the polymerization of DMAA provided additional free DEPN was introduced in the bulk. The latter observation, along with the required initial nitroxide excess involved in several polymerization systems, is consistent with the role played by excess nitroxide in the field of NMRP, as long

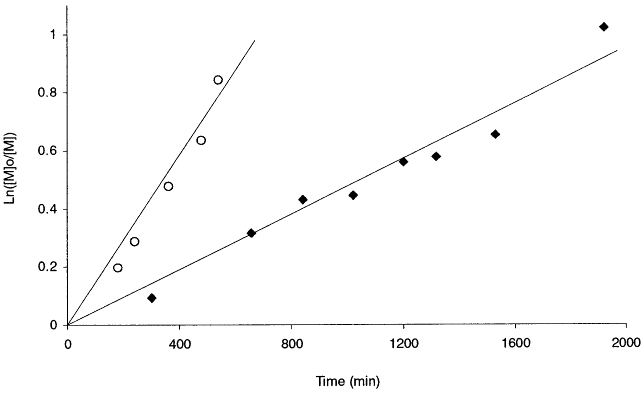


**Figure 4.** Bulk polymerization of DMAA at 110 °C; $\ln([\mathrm{M}]_0/[\mathrm{M}])$ vs time. System I (○): $[\mathrm{DEPN}]_0/[\mathrm{AIBN}]_0 = 2$; $[\mathrm{AIBN}]_0 = 2.2 \times 10^{-2}$ mol.L$^{-1}$; overall nitroxide concentration $= 4.4 \times 10^{-2}$ mol L$^{-1}$. System II (◆): $[\text{alkoxyamine}]_0 = 2.2 \times 10^{-2}$ mol L$^{-1}$; $[\text{excess free DEPN}]_0 = 0.66[\text{alkoxyamine}]_0$; overall nitroxide concentration $= 3.5 \times 10^{-2}$ mol L$^{-1}$.

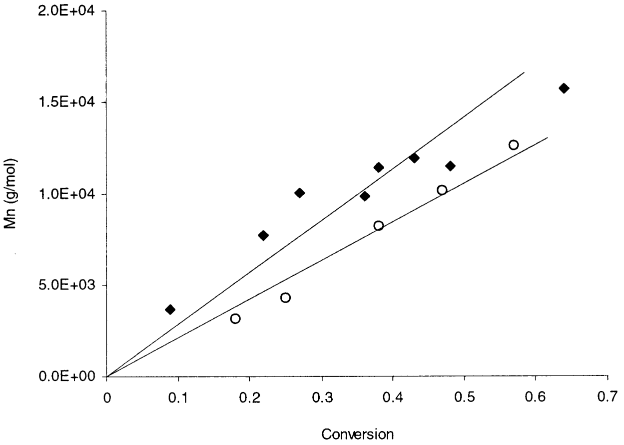


**Figure 5.** Bulk polymerization of DMAA at 110 °C; $M_n$ vs conversion. System I (○): $[\mathrm{DEPN}]_0/[\mathrm{AIBN}]_0 = 2$; $[\mathrm{AIBN}]_0 = 2.2 \times 10^{-2}$ mol L$^{-1}$; overall nitroxide concentration $= 4.4 \times 10^{-2}$ mol L$^{-1}$. System II (◆): $[\text{alkoxyamine}]_0 = 2.2 \times 10^{-2}$ mol L$^{-1}$; $[\text{excess free DEPN}]_0 = 0.66[\text{alkoxyamine}]_0$; overall nitroxide concentration $= 3.5 \times 10^{-2}$ mol L$^{-1}$.

underlined by Georges et al.[5] and more recently by Lacroix-Desmazes et al.[43] This finally led us to work with an alkoxyamine original concentration equal to 2.2 $\times 10^{-2}$ mol L$^{-1}$ and a 66% DEPN molar excess, which means that the potential DEPN overall concentration (free DEPN + alkoxyamine) was 3.65 $\times 10^{-2}$ mol L$^{-1}$.

The obtained $M_n$ vs conversion plot (Figure 5) is consistent with these concentration values: System I, with a higher original nitroxide concentration, turned to yield polymers with lower molar weights than system II for the same conversion.

Compared to former nitroxides that had been reported for the NMRP of DMAA,[25,39,41] DEPN enabled to largely extend the range of polymerization control (from 10% to almost 60% conversion). For 57% conversion (after less than 9 h polymerization) and under the experimental conditions described in Table 3, the number-average molecular weight of poly(DMAA) was 12 600 g mol$^{-1}$ with a polydispersity of 1.39 (poly(2VP) calibration). As for 4VP, the original nitroxide concentration proved responsible for the number of growing chains. Indeed, as shown in Table 3, the experimental number-average molar weights were closer to the theoretical ones that had been worked out when considering the initial overall DEPN concentration (alkoxyamine + free DEPN) than to those calculated from the original concentration of the initiating species.

**Table 3. Bulk Polymerization of DMAA at 110 °C Using Systems I and II**

| conv | theor $M_n$ ($10^3$ g/mol) | $M_n$ ($10^3$ g/mol) (poly(2VP) standards) | $M_w/M_n$ (poly(2VP) standards) |
|---|---|---|---|
| 0.18[a] | 3.9,[c] 3.9[d] | 3.1 | 1.37 |
| 0.25[a] | 5.4,[c] 5.4[d] | 4.3 | 1.45 |
| 0.38[a] | 8.3,[c] 8.3[d] | 8.2 | 1.26 |
| 0.47[a] | 10.4,[c] 10.4[d] | 10.2 | 1.27 |
| 0.57[a] | 12.7,[c] 12.7[d] | 12.6 | 1.39 |
| 0.09[b] | 3.9,[c] 2.4[d] | 3.7 | 1.41 |
| 0.22[b] | 9.6,[c] 5.8[d] | 7.6 | 1.31 |
| 0.27[b] | 11.6,[c] 7.0[d] | 10.0 | 1.21 |
| 0.36[b] | 15.8,[c] 9.5[d] | 9.8 | 1.37 |
| 0.38[b] | 16.3,[c] 9.8[d] | 11.4 | 1.31 |
| 0.43[b] | 19.3,[c] 11.6[d] | 11.9 | 1.35 |
| 0.48[b] | 21.2,[c] 12.8[d] | 11.5 | 1.38 |
| 0.64[b] | 28.4,[c] 17.1[d] | 15.7 | 1.54 |

[a] $[\mathrm{DEPN}]_0/[\mathrm{AIBN}]_0 = 2$; $[\mathrm{AIBN}]_0 = 2.2 \times 10^{-2}$ mol L$^{-1}$; overall nitroxide concentration $= 4.4 \times 10^{-2}$ mol L$^{-1}$. [b] $[\text{Alkoxyamine}]_0 = 2.2 \times 10^{-2}$ mol L$^{-1}$; $[\text{excess free DEPN}]_0 = 0.66[\text{alkoxyamine}]_0$; overall nitroxide concentration $= 3.5 \times 10^{-2}$ mol L$^{-1}$. [c] Considering the original concentration of the initiating species as determining. [d] Considering the original overall nitroxide concentration (DEPN + alkoxyamine) as determining.

**Table 4. Comparison between the Experimentally Obtained Values of Both Molar Weights and Polydispersities Depending on the Standards Used To Calibrate the SEC Column**

| $M_n$ ($10^3$ g/mol) (polystyrene standards) | $M_n$ ($10^3$ g/mol) (poly(2VP) standards) | $M_w/M_n$ (polystyrene standards) | $M_w/M_n$ (poly(2VP) standards) |
|---|---|---|---|
| | Poly(4VP) | | |
| 44.7 | 13.6 | 1.05 | 1.12 |
| 48.0 | 14.9 | 1.05 | 1.12 |
| 52.3 | 17.2 | 1.04 | 1.10 |
| 53.8 | 17.8 | 1.04 | 1.10 |
| 59.3 | 20.9 | 1.05 | 1.11 |
| 60.5 | 21.1 | 1.05 | 1.14 |
| 61.2 | 24.2 | 1.14 | 1.20 |
| 65.7 | 24.4 | 1.03 | 1.09 |
| 71.7 | 27.1 | 1.08 | 1.21 |
| 73.0 | 28.4 | 1.05 | 1.13 |
| 81.4 | 32.2 | 1.12 | 1.28 |
| 92.9 | 39.7 | 1.12 | 1.27 |
| 98.4 | 44.3 | 1.11 | 1.23 |
| 105.2 | 47.5 | 1.15 | 1.31 |
| 123.8 | 60.6 | 1.09 | 1.15 |
| | Poly(DMAA) | | |
| 20.7 | 3.7 | 1.13 | 1.41 |
| 22.9 | 4.3 | 1.19 | 1.45 |
| 26.2 | 5.3 | 1.12 | 1.36 |
| 30.8 | 7.0 | 1.11 | 1.33 |
| 32.3 | 7.7 | 1.09 | 1.31 |
| 35.1 | 8.6 | 1.13 | 1.39 |
| 37.9 | 10.0 | 1.07 | 1.21 |
| 42.8 | 11.9 | 1.13 | 1.35 |
| 46.5 | 13.3 | 1.15 | 1.43 |

To allow a better comparison of the properties of our systems with those of others reported in the literature on the basis of polystyrene standards, the characteristics of the molar weight distributions of poly(DMAA) and poly(4VP) were also determined using a polystyrene standard calibration (Table 4). As expected given the very different polarities of polystyrene, polyvinylpyridine, and the highly polar eluent (DMF) used for the SEC analysis, the results concerning poly(4VP) indicated that a polystyrene calibration overestimated 2−3 times the number-average molar weights of poly(4VP) samples and, at the same time, underestimated their

**Table 5. Features of the Different Copolymers Obtained with Each Type of Nitroxide**

| nature of the used nitroxide | $M_n$ ($10^3$ g/mol) (poly(2VP) standards) | $M_w/M_n$ (poly(2VP) standards) | molar percentage of 4VP units | molar percentage of DMAA units |
|---|---|---|---|---|
| DEPN[a] | 25.4 | 1.23 | 0 | 100 |
| | 29.6 | 1.21 | 15 | 85 |
| | 36.4 | 1.23 | 30 | 70 |
| | 39.9 | 1.23 | 36 | 64 |
| | 52.2 | 1.40 | 51 | 49 |
| TEMPO[b] | 7.8 | 1.53 | 50 | 50 |
| | 7.6 | 1.61 | 51 | 49 |
| | 7.3 | 1.61 | 53 | 47 |
| | 6.8 | 1.61 | 57 | 43 |
| | 6.5 | 1.55 | 60 | 40 |
| | 5.7 | 1.83 | 68 | 32 |
| | 3.9 | 1.37 | 100 | 0 |

[a] Using a poly(DMAA) macroinitiator along with DEPN to copolymerize 4VP. [b] Using a poly(4VP) macroinitiator along with TEMPO to copolymerize DMAA.

polydispersities. This trend got even worse in the case of poly(DMAA), for which poly(2VP) and polystyrene calibrations yielded molar weights that differed by 3−6-fold, while polydispersity indices—which could be regarded as satisfactory using polystyrene standards—dramatically increased when using poly(2VP) standards, while still remaining below the critical limit of 1.5 obtained for a standard radical polymerization. Furthermore, it must be pointed out that using poly(DMAA) standards would probably increase such differences. Although it is well-known that the characterization of polymers by SEC on the basis of relative calibration is highly dependent on the standards that are used to calibrate the column, very little apart from the very recent paper by Charleux et al.[17] has been reported in the NMRP literature so far about the influence of the choice of the standards on polydispersity values (which are among the key factors to assess the controlled character of any polymerization). Our results clearly show that, in certain conditions, a SEC analysis based on a polystyrene calibration (as most commonly reported in the literature on controlled radical polymerization) can convey a somewhat idealized assessment of the molecular weight distribution by overestimating its homogeneity.

**Synthesis of Poly(DMAA-*b*-4VP) Block Copolymers.** As previously mentioned, TEMPO had already enabled us to synthesize block copolymers with 4VP and DMAA units, but the size of the second block (i.e., hydrophilic poly(DMAA)) was rather small compared with that of the first block (i.e., poly(4VP)). Furthermore, if the number-average molar weights of the obtained macromolecules had appeared satisfactory when worked out from polystyrene standards, they turned to appear rather small once poly(2VP) standards were used to calibrate the SEC column. As regards polydispersity values, they turned from inferior to 1.5 using a polystyrene calibration to sometimes superior to 1.5 when obtained from poly(2VP) standards (see this work) (Table 5).

On the other hand, the use of DEPN led to longer hydrophilic poly(DMAA) blocks with a much better reaction control. The latter was then used as a macroinitiator for the chain extension by 4-vinylpyridine whose polymerization was much easier to control than that of DMAA. As shown by Figures 6 and 7, the polymerization of the second block poly(4VP) was also very well controlled.

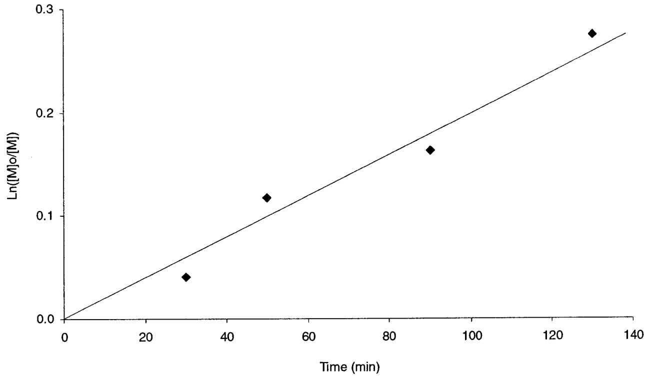


**Figure 6.** Copolymerization of 4VP at 110 °C using a poly(DMAA) macroinitiator ($M_n$ = 25 400 g mol$^{-1}$; $M_w/M_n$ = 1.23); ln([4VP]$_0$/[4VP]) vs time; [macroinitiator]$_0$ = 8.5 × $10^{-3}$ mol L$^{-1}$.

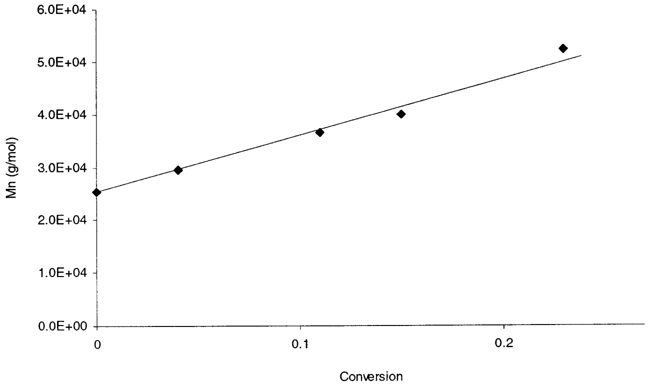


**Figure 7.** Copolymerization of 4VP at 110 °C using a poly(DMAA) macroinitiator ($M_n$ = 25 400 g.mol$^{-1}$; $M_w/M_n$ = 1.23); $M_n$ vs 4VP conversion; [macroinitiator]$_0$ = 8.46 × $10^{-3}$ mol L$^{-1}$.

As shown in Table 5, DEPN led to satisfactory molar weights for both blocks and also allowed to complete the range of synthesized copolymers by more hydrophilic species, which was one of the objectives of this work.

## Conclusions

The reported results have brought an interesting insight into nitroxide-mediated radical polymerizations and have first revealed the good performance of DEPN for the NMRP of two functional and polar monomers.

The bimolecular system DEPN/AIBN (2/1) as well as alkoxyamine Sty-DEPN based systems enabled to control the radical polymerization of *N*,*N*-dimethylacrylamide (DMAA) and 4-vinylpyridine (4-VP). For both investigated monomers, and particularly for DMAA, the progress was really significant as compared with the results formerly obtained with TEMPO: a 30 °C lower temperature, much shorter polymerization times (i.e., at least 20 times shorter for DMAA), high conversion for NMRP (even superior to 60%), higher average molecular weights, etc.

The good control obtained for both radical homopolymerizations allowed the consecutive synthesis of poly(DMAA)-*b*-poly(4-VP) block copolymers from a poly(DMAA) macroinitiator. Even during chain extension, the control of the radical polymerization of 4VP proved excellent, and a wide range of well-defined block copolymers were eventually obtained. In addition to covering a much broader composition range than that formerly obtained with TEMPO, the new family of block copolymers also displayed much higher average molar weights for both blocks.

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MA0260086