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Nitroxide-Mediated Radical Polymerization of 4-Vinylpyridine: Study of the Pseudo-Living Character of the Reaction and Influence of Temperature and Nitroxide Concentration

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ABSTRACT: The free radical polymerization of 4-vinylpyridine (4VP), using 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) radical as a capping agent, proved to proceed in a pseudo-living manner, providing low polydispersity P4VP whose chain growth could be controlled. The original nitroxide concentration was revealed to have no obvious influence on the rate of polymerization, whereas it could be directly related to the molecular weight of the polymer. The polydispersity was shown to increase within the range 1.02−1.50. The influence of temperature on the kinetics of the reaction was demonstrated, but no significant effect could be found on the molecular weights and polydispersities of the macromolecules.

Introduction

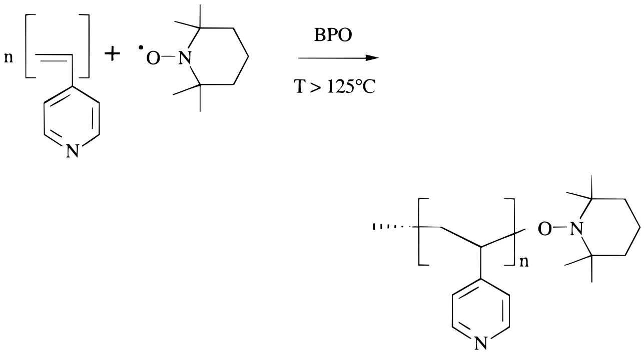
Combining the advantages of both ionic and radical polymerizations (ability to generate polymers with controlled architectures/nondemanding experimental conditions), pseudo-living free radical polymerization has been the focus point of a growing concern for the last 20 years, more particularly since the work of Rizzardo.[1] More recently, Georges et al.[2] emphasized the advantages of the use of nitroxide radicals as controlling agents, thus developing a new method called nitroxide-mediated radical polymerization (NMRP). Nitroxide radicals have proved to be able to protect the active center of each growing chain by capping it, occasionally releasing it to permit the insertion of a monomer unit. This mechanism involves the equilibrium which occurs between dormant species called adducts and active species (i.e. growing radicals).

Although NMRP was originally devoted to studies concerning styrene, it progressively expanded toward acrylates and methacrylates, while some authors attempted to polymerize more exotic monomers.[3] Surprisingly, 4-vinylpyridine had never been examined as a potential monomer for controlled free radical polymerization before the works of Bohrisch et al.[4] Considering that the nitrogen atom of the pyridine ring could be quaternized and, thus, yield molecules which are useful in the field of amphiphilic polymers which has long been investigated in our laboratory,[5−7] we decided to conduct further research to adapt NMRP to our objectives. More precisely, as far as amphiphilic polymers are concerned, the macromolecular properties can mainly be modulated by synthesizing copolymers with good structural control, which was thought to be achievable by using NMRP. In that perspective, this work is a preliminary study concerning the ability of 4VP as a monomer to be polymerized in a controlled manner.

Experimental Section

Materials. Commercial 4-vinylpyridine (Aldrich) was distilled under reduced pressure (62−65 °C/15 mmHg). Commercial 2,2,6,6-tetramethylpiperidin-1-oxyl (Aldrich) was used as received, and benzoyl peroxide (BPO) was recrystallized from methanol/chloroform.

Scheme 1. Polymerization of 4-Vinylpyridine Using TEMPO and Benzoyl Peroxide



Synthesis of P4VP. Typically, a 100 mL, two-necked round-bottom flask equipped with an argon gas purge, a reflux condenser, a magnetic stirrer, and a temperature-control device, was charged with 4 mL of 4-vinylpyridine and different amounts of TEMPO, depending on the experiment. The solution was then immersed in a preheated oil-bath which ensured a temperature of 138 °C in the reactor. After 10 min, benzoyl peroxide was introduced, and the mixture was left to polymerize. The amounts of TEMPO and benzoyl peroxide were calculated so as to be in a molar ratio TEMPO/BPO equal to 1.3/1 according to the literature.[8] After the required duration, the reaction was stopped by cooling the flask. The obtained polymer was recovered by evaporating excess monomer and carefully dried under vacuum (0.5 mmHg) at 60 °C for 2 days.

Size Exclusion Chromatography (SEC). Prior to any experiment, the polymers were left to dissolve for 24 h in dimethylformamide (DMF 99.5%), which was also to be used as eluent (elution rate: 1 mL/min). Before injection, the solutions were filtered through PTFE membranes (Alltech; pore diameter: 200 nm). The temperature was maintained at 35 °C during all SEC experiments. Measurements were performed on a Waters device equipped with a Styragel HR4 7.8 × 300 mm column (10^3 to 5×10^6 g/mol). The system had previously been calibrated with standard polystyrenes purchased from Polymer Standard Service. Sample detection was

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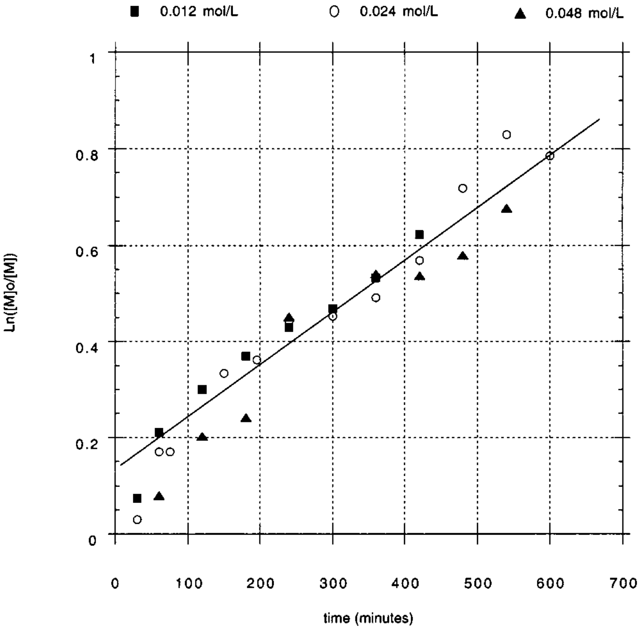


Figure 1. Bulk polymerization of 4-vinylpyridine at 138 °C using different nitroxide concentrations: ln($[M]_0/[M]$) vs *t*, [M] = monomer concentration; $[TEMPO]_0 = 1.2 \times 10^{-2}$, 2.4×10^{-2}, and 4.8×10^{-2} mol/L.

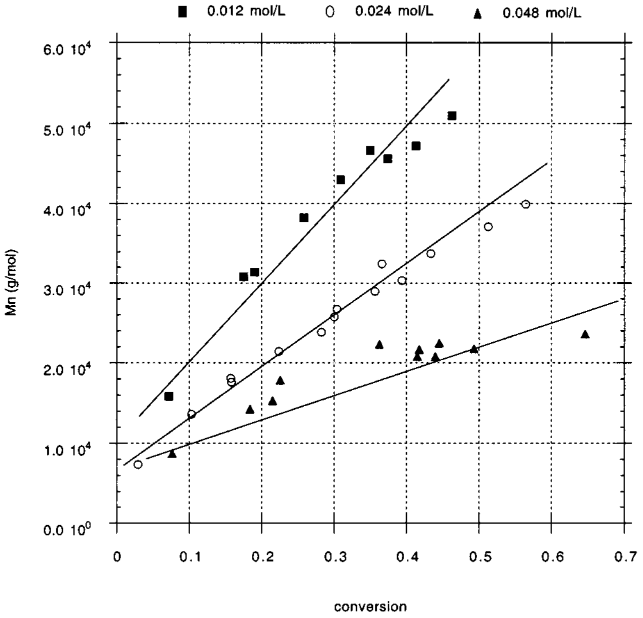


Figure 2. Bulk polymerization of 4-vinylpyridine at 138 °C using different nitroxide concentrations: M_n vs conversion; $[TEMPO]_0 = 1.2 \times 10^{-2}$, 2.4×10^{-2}, and 4.8×10^{-2} mol/L.

Table 1. Molecular Weights and Polydispersities of Some Polymers, As Estimated by SEC after Calibration Using Polystyrene ($[TEMPO]_0 = 2.4 \times 10^{-2}$ mol/L; $T = 138$ °C)

polymerization time (min)	ln($[M]_0/[M]$)	conversion	M_n	M_w/M_n
30	0.030	0.029	7 300	1.02
60	0.171	0.158	17 600	1.07
150	0.333	0.283	23 900	1.11
195	0.362	0.304	26 800	1.22
240	0.440	0.356	29 000	1.23
420	0.569	0.434	33 700	1.28
480	0.719	0.513	37 100	1.37
540	0.829	0.564	39 900	1.38

done with a Waters 410 differential refractometer. The results were processed using Millenium software.

Results and Discusssion

Scheme 1 depicts the polymerization of 4VP using benzoyl peroxide as an initiator and TEMPO as a capping agent. The data related to the molecular weights and polydispersities of some of the P4VPs, as characterized by SEC, have been gathered in Table 1.

One of the features of “living” radical polymerization is that the number of active species is almost constant throughout the reaction. This point can be evidenced by plotting the value ln($[M]_0/[M]$) as a function of time, $[M]_0$ and [M] respectively standing for the original and current monomer concentrations in the bulk (as estimated by their proportionality with the weight of formed polymer). In the case of 4-vinylpyridine, Figure 1 clearly demonstrates that ln($[M]_0/[M]$) vs *t* is nearly a straight line. Furthermore, it is to be noticed that the initial nitroxide concentration has no real influence on the polymerization rate since the values obtained for different nitroxide concentrations are all on the same straight line. A similar observation was made by Catala et al.[9] concerning the polymerization of *p*-*tert*-butylstyrene. Matyjaszewski[10,11] and Fukuda[12,13] explained this phenomenon on a larger scale: because TEMPO is added in excess, all radicals arising from BPO are capped by the nitroxide very early. Thus, a majority of chains are terminated by a TEMPO moiety throughout the reaction. Growing radicals can only be provided by autoinitiation, which maintains a reasonable polymerization rate and counterbalances irreversible termination. It is to be noticed that TEMPO moieties exchange between the formerly capped chains and the uncapped radicals generated by autoinitiation. This overall mechanism accounts for the fact that the polymerization rate is governed by autoinitiation and not by the nitroxide concentration. Thus, in the case of the TEMPO-mediated polymerization of 4-vinylpyridine, the kinetic features of the reaction are unchanged when TEMPO concentration is doubled or even multiplied 4-fold ($[TEMPO]_0$ varying from 1.2×10^{-2} to 2.4×10^{-2} mol/L and even to 4.8×10^{-2} mol/L).

Beside the almost complete disappearance of irreversible bimolecular terminations, pseudo-living radical polymerization presents a drastic limitation of transfer reactions. The achievement of this condition can be checked by plotting the molecular weight of the obtained polymer as a function of conversion. As a matter of fact, the lower the number of transfer reactions, the more linear the plot. Figure 2 highlights the evolution of M_n vs conversion for the polymerization of 4VP at 138 °C using different nitroxide concentrations. In all cases, the plots are almost straight lines as long as conversion remains moderate. Yet, this linear behavior becomes less obvious when monomer consumption reaches high percentages. Thus, the lines obtained for $[TEMPO]_0 = 1.2 \times 10^{-2}$ mol/L and $[TEMPO]_0 = 4.8 \times 10^{-2}$ mol/L in particular present substantial curvature for conversions exceeding 0.4.

Figure 2 also demonstrates that the final structure of the macromolecules is directly related to the original nitroxide concentration: one molecule of TEMPO terminates one active polymeric radical, because, for instance, the concentration of residual TEMPO during the polymerization of styrene is approximately 0.1−1% of the initial concentration[10] and, thus, more than 99% chains are capped by a nitroxide. As a consequence, for an identical conversion, i.e. for the same monomer

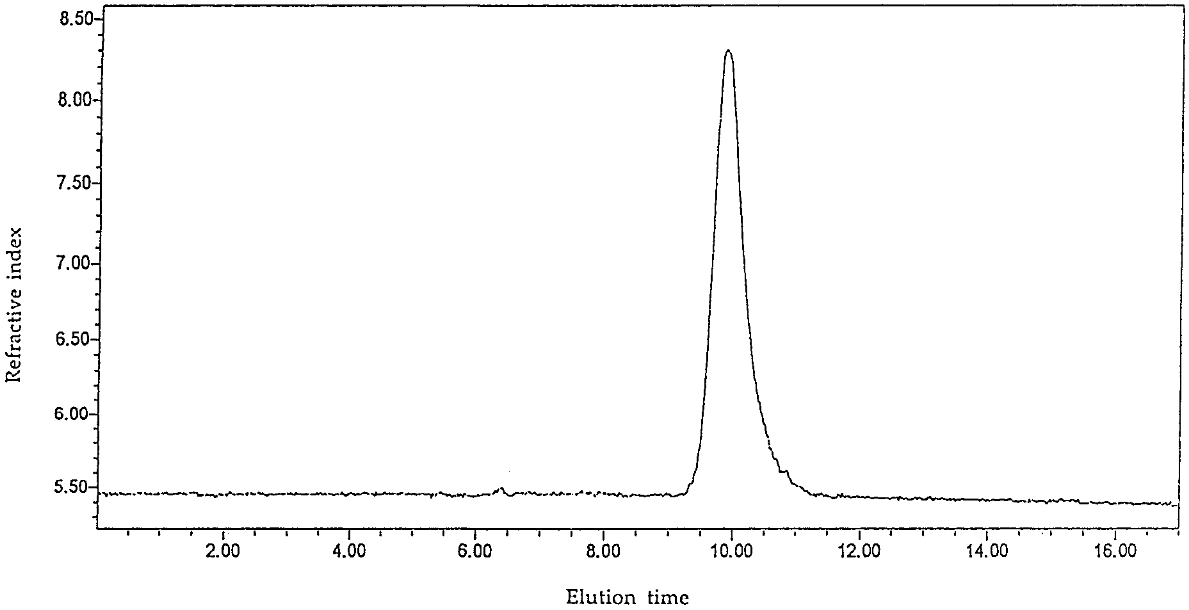
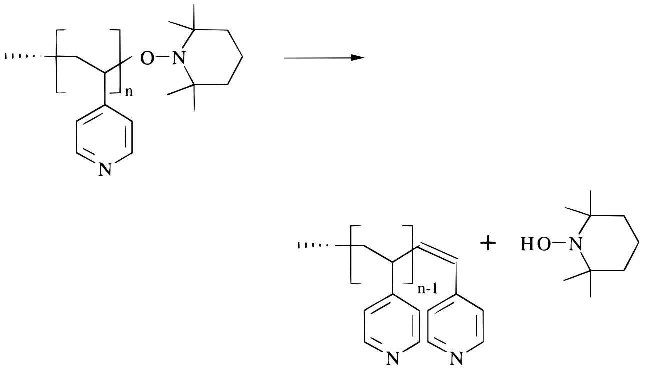


Figure 3. Typical size exclusion chromatogram.

Scheme 2. Thermal Decomposition of the Terminal C−TEMPO Bond



consumption, the higher the original nitroxide concentration, the lower the molecular weights of the resulting polymers. Indeed, the same amount of monomer is supposed to supply the growth of a higher number of active species. The three curves clearly indicate that an increase in the initial TEMPO concentration triggers a decrease in the final average molecular weight. However, the molecular weights are not exactly doubled when $[\mathrm{TEMPO}]_0$ is halved, or quadrupled when $[\mathrm{TEMPO}]_0$ is divided by four. In that perspective, it is also worth noticing that the obtained molecular weights are not exactly the same as those expected by calculation, which would somehow indicate that not all polymers have a TEMPO moiety at the chain-end. As reported in the literature,[10] the destruction of TEMPO activity due to the abstraction of a hydrogen atom by the terminal TEMPO group (Scheme 2) might take part in the discrepancy between the ideal case (i.e. a one-to-one ratio for TEMPO radicals and growing chains) and the experimental results.

One of the typical interests of NMRP is undoubtedly the opportunity to yield polymers with a very low polydispersity (M_w/M_n), sometimes even as low as the one reached when ionic polymerizations are used. An example of this low polydispersity is given in Figure 3 with a curve obtained during our SEC experiments. The results concerning the polydispersity indices are gathered in Figure 4, which shows that very good M_w/M_n values can be obtained by polymerizing 4VP in the presence of TEMPO as a control agent. Indeed, whatever the initial concentration of TEMPO, M_w/M_n ranges from 1.02 to 1.5. According to Greszta and Matyjaszewski,[10] the increase in polydispersity as a function of conversion is not unexpected. Indeed, the decomposition of the terminal C−TEMPO bond, which occurs during the reaction, diminishes the overall potentially available amount of TEMPO. This phenomenon affects the growth control and, thus, the molecular weight distribution. Figure 4 also demonstrates the influence of the initial nitroxide concentration on polydispersity. Logically, the higher the former is, the closer to 1 the latter is.

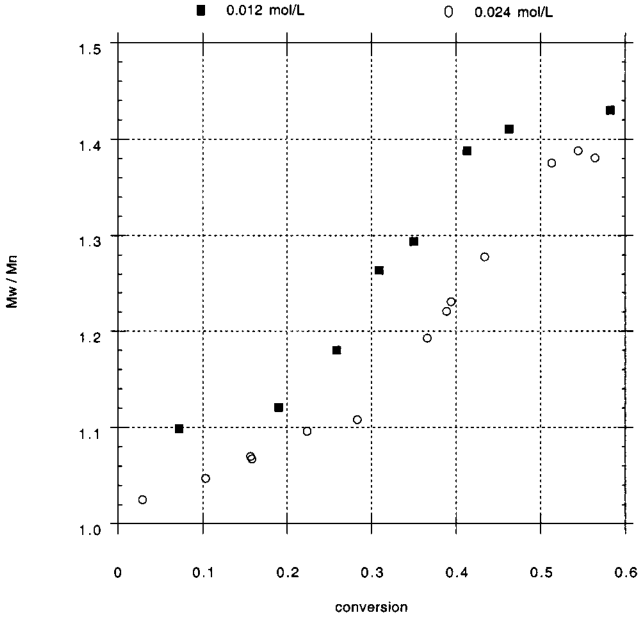


Figure 4. Bulk polymerization of 4-vinylpyridine at 138 °C using different nitroxide concentrations: M_w/M_n vs conversion; $[\mathrm{TEMPO}]_0 = 1.2 \times 10^{-2}$ and 2.4×10^{-2} mol/L

The influence of temperature on the kinetics of the reaction was studied for an original nitroxide concentration which was equal to 2.4×10^{-2} mol/L. The results have been gathered in Figure 5. It is to be noticed that the curves plotting $\ln([M]_0/[M])$ vs t are all straight lines.

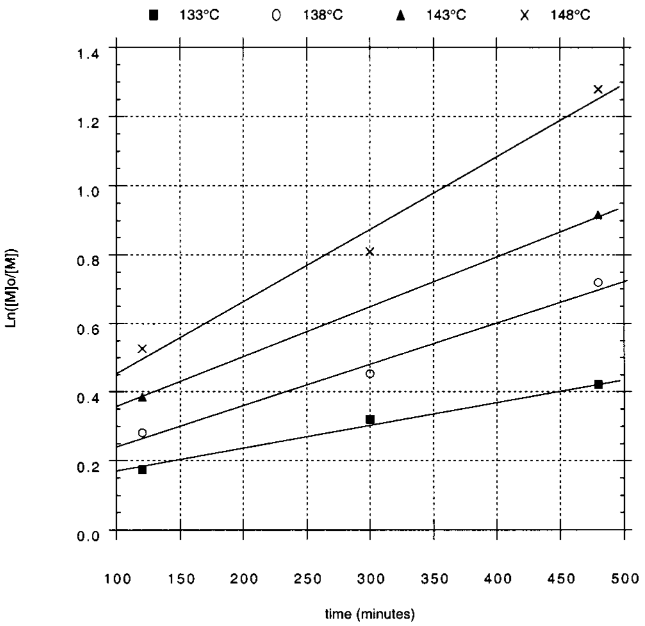


Figure 5. Bulk polymerization of 4-vinylpyridine. Influence of temperature on the kinetics of the reaction. $[\mathrm{TEMPO}]_0 = 2.4 \times 10^{-2}$ mol/L.

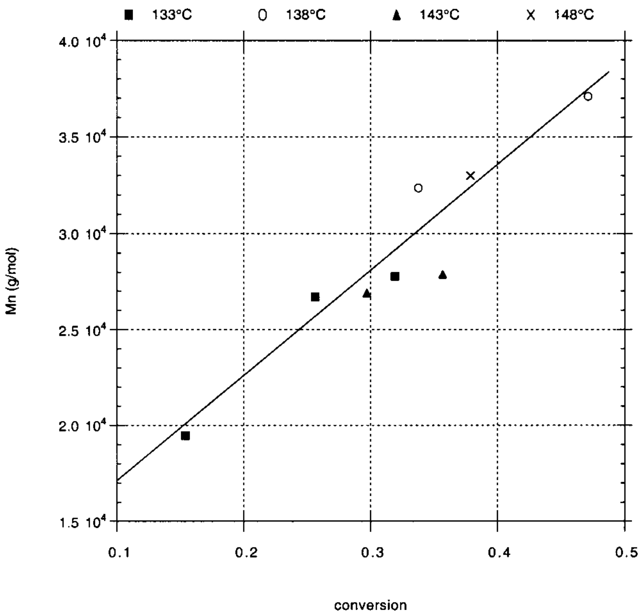


Figure 6. Bulk polymerization of 4-vinylpyridine. Influence of temperature on the structure of the obtained polymers. $[\mathrm{TEMPO}]_0 = 2.4 \times 10^{-2}$ mol/L.

As expected, the corresponding slope values increase with temperature, which clearly means that an increase in temperature immediately provokes an acceleration of the polymerization. Taking into account the very small differences in temperature among our experiments, it is particularly remarkable that the kinetic parameters are so sensitive to the experimental conditions. Indeed, even a simple 5 deg difference can cause a striking response in the slope, i.e. in the $k_p[R^*]$ value (which equals $R_p/[M]$, where R_p stands for the overall polymerization rate). Contrary to the rate of polymerization, the features (i.e. M_n, M_w/M_n) of the obtained polymers do not seem to be influenced much by slight differences in temperature. As an example, Figure 6 exhibits the macromolecular weights of some of the P4VPs synthesized under the conditions mentioned above ($T = 133$, 138, 143, and 148 °C). All points tend to be aligned on the same curve, whatever the temperature, as long as the initial nitroxide concentation remains constant (in our case, $[\mathrm{TEMPO}]_0 = 2.4 \times 10^{-2}$ mol/L).

Conclusions

According to our experiments, the nitroxide-mediated free radical polymerization of 4-vinylpyridine proceeds in a pseudo-living manner. Consequently, it is possible to control the features of the final P4VP macromolecules. Indeed, providing monomer consumption is kept within a certain range, molecular weights increase linearly with conversion and polydispersities remain low (1.02−1.5), which yields molecular weight distributions as narrow as those obtained by ionic polymerizations. Further studies are now underway to highlight the possible use of the active chain end of dormant P4VPs when involved in a copolymerization process, with a view to synthesizing amphiphilic polymers with a well-defined structure. Indeed, previously synthesized P4VP radicals are likely to grow into a well-structured block copolymer when used as both macroinitiators and control agents (the equilibrium between dormant and active species may release a polymeric radical as well as a TEMPO radical) in the presence of a second monomer.

References and Notes

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