Behavior of 3-Vinylpyridine in Nitroxide-Mediated Radical Polymerization: The Influence of Nitroxide Concentration, Solvent, and Temperature

XING ZHE DING,[1] ARNAUD FISCHER,[1] ALAIN BREMBILLA,[2] PIERRE LOCHON[1]

[1] Laboratoire de Chimie-Physique Macromoléculaire, UMR CNRS-INPL 7568, Groupe ENSIC, 1, rue Grandville, BP 451, 54001 Nancy Cedex, France

[2] Laboratoire d'Etude des Systèmes Organiques et Colloïdaux, UMR CNRS-UHP Nancy I 7565, BP 239, 54506 Vandoeuvre-les-Nancy Cedex, France

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ABSTRACT: The influence of nitroxide concentration, solvent, and temperature on the nitroxide-mediated radical polymerization of 3-vinylpyridine (3VP) was examined. Long-chain poly(3-vinylpyridine)s with low polydispersities were synthesized. The initial 2,2,6,6-tetramethylpiperidin-1-oxyl concentration had no influence on the kinetics of the polymerization but was responsible for the obtained molar weights. Compared with the polymerization of styrene, the polymerization of 3VP proved quite fast. The influence of temperature on the reaction rate was also demonstrated, and the polymerization could be controlled even at 110 °C. Some polymerizations were also performed in solution to test the influence of a solvent such as ethylene–glycol, whose effect on the polymerization of 3VP was dependent on temperature. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 3067–3073, 2000

Keywords: 3-vinylpyridine; nitroxide; controlled radical polymerization

INTRODUCTION

For a few years now, and especially since the pioneering work of Rizzardo,[1] controlled radical polymerization has become the focus point of a growing interest. This technique can yield polymers with controlled architectures and narrow molar weight distributions such as those obtained by ionic polymerizations but without demanding experimental conditions. In 1993, Georges et al.[2] emphasized the behavior of nitroxide radicals as potential control agents, thus developing a new method called *nitroxide-mediated radical polymerization* (NMRP). This method is based on the existence of dormant species, called *adducts*, which are formed by the reversible association of the growing polymeric radical with a nitroxide. The theoretical scheme has been extensively studied, mainly by Georges,[3,4] Fischer,[5,6] Matyjaszewski,[7–11] and Fukuda.[12–14] All radicals generated by the decomposition of the initiator are very quickly transformed into dormant species by nitroxide capping, and the radical concentration in the bulk is very low, which reduces transfer reactions as well as irreversible termination reactions due to bimolecular combination. Autoinitiation is supposed to ensure that a sufficient amount of radicals is always present in the medium to enable the polymerization to go on at a reasonable rate. Newly formed radicals are capped by nitroxide moieties that stem from the reversible dissociation of formerly existing adducts. The propagation itself is allowed because its rate is at least equal to the exchange rate.

NMRP represents a very interesting route to synthesizing polymers with a precisely controlled

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Correspondence to: A. Fischer (E-mail: Arnaud.Fischer@ensic.inpl-nancy.fr)

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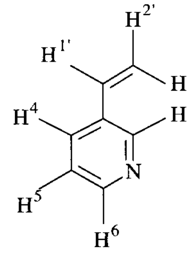
size and was originally devoted to studies concerning industrial monomers, such as styrene, acrylates, and methacrylates. However, even though new nitroxides[15,16] have triggered recent interest, the field of new monomers different from styrene and its derivatives that can be polymerized in the presence of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) has scarcely been broadened. Among them, 4-vinylpyridine (4VP) has recently been studied.[17,18] Its free-radical polymerization with TEMPO as a capping agent proceeds in a pseudoliving manner, providing low-polydispersity (1.05–1.50) poly(4-vinylpyridine)s whose chain growth can be controlled. Whatever the position of the vinyl substituent, vinylpyridines bear a nucleophilic basic nitrogen atom that can be quaternized, providing interesting amphiphilic species.[19,20] In that perspective, controlled radical polymerization reveals a very accurate means of obtaining new amphiphilic cationic copolymers with a block structure whose behavior is likely to depend on the position of the nitrogen atom with respect to the main chain. Before the synthesis of block copolymers, it was interesting to investigate the behavior of 3-vinylpyridine (3VP) in terms of bulk NMRP, which is the first objective of this article. Indeed, compared to its homologue 4VP, 3VP presents a different polarization of the polymerizable group. The electronic distribution on the pyridinic ring, along with resonance effects, may influence the dissociation of the C—TEMPO bond and, consequently, the kinetics of the overall polymerization. A substantial part of this work is also devoted to the study of the reaction in a high-boiling-point solvent, ethylene–glycol, because of the interest in solvents in this type of polymerization. As a matter of fact, solvents enable the reaction to be conducted without any limitation in conversion for polymers with a high glass-transition temperature and for which bulk polymerization might result in early precipitation or the formation of an extremely viscous mixture. Furthermore, solvents also allow the use of high-melting-point monomers (e.g., salts) in the fields of homopolymerization and copolymerization.

EXPERIMENTAL

Materials

Commercial TEMPO (Aldrich) was used as received, and benzoyl peroxide (BPO) was recrystallized from methanol/chloroform. 4VP was purchased from Aldrich and distilled under reduced pressure (bp = 62–65 °C/15 mmHg) to remove the stabilizer.



Scheme 1. Protons of 3VP.

Synthesis of 3VP

After the improvement of a previously described method,[21,22] 3VP was synthesized via a Wittig reaction. Typically, in a 500-mL, three-necked, round-bottom flask, to 0.112 mol of methyl triphenylphosphonium bromide (98%; Aldrich) dissolved in 400 mL of anhydrous tetrahydrofuran (99.9%; Aldrich), there was added 0.224 mol of sodium hydride (60% dispersed in mineral oil; Aldrich) under argon at 0 °C. After 2 h, 0.1 mol of 3-pyridine-carboxaldehyde (98%; Aldrich) was added dropwise. The mixture was then left under constant stirring at 25 °C for 12 h. Excess ylide was destroyed with the addition of acetone. The mixture was then filtered, and the filtrate was concentrated by rotative evaporation. 3VP was extracted with diethyl ether. Further purification consisted of two distillations of the liquid (bp = 70–71 °C/15 mmHg) on calcium hydride, the second distillation being conducted immediately before use. The purity of the monomer was checked by ^{1}H NMR (200 MHz) in $CDCl_3$ (Scheme 1): $\delta = 8.59$ [2, $J(2,4) = 2.33$], 8.46 [dd, 6, $J(6,5) = 4.81$], 7.69 [m, 4, $J(4,6) = 1.63$, $J(4,5) = 7.89$], 7.22 [o, 5, $J(5,2) = 1.25$], 6.67 [dd, 1′, $J(1',2') = 11$, $J(1',3') = 17.7$], 5.8 [dd, 3′, $J(3',1') = 17.7$], 5.35 ppm [dd, 2′, $J(2',3') = 0.7$]. The refractive index was $n_D^{25} = 1.5460$.

Polymerization

Typically, a 50-mL reactor was charged with 4 mL of monomer (37.1 mmol), 0–29.8 mg (0.019 mmol) of TEMPO, and 0–35 mg (0.015 mmol) of BPO as an initiator. According to the literature,[23] the TEMPO/BPO molar ratio was equal to 1.3/1. The mixture was degassed by several freeze–thaw cycles and finally left under argon. The vessel was then immersed in a preheated oil bath. Magnetic

Table I. Characteristics of a Few Polymerizations of 3VP

T (°C)	$[TEMPO]_0$ ($\times 10^2$ mol/L), $[BPO]_0$ ($\times 10^2$ mol/L)	Solvent	Time (h)	Conversion	Polystyrene-Equivalent M_n (g/mol)	M_w/M_n
138	1.2, 0.9	/	0.5	0.38	96,900	1.10
138	1.2, 0.9	/	1	0.49	99,500	1.22
138	1.2, 0.9	/	1.5	0.61	108,200	1.25
138	2.4, 1.8	/	0.5	0.37	73,200	1.08
138	2.4, 1.8	/	1	0.51	81,900	1.12
138	2.4, 1.8	/	2	0.72	97,400	1.14
138	4.8, 3.7	/	0.5	0.34	51,400	1.07
125	2.4, 1.8	/	1	0.09	41,600	1.10
125	2.4, 1.8	/	2	0.19	59,400	1.08
125	2.4, 1.8	/	4	0.44	90,300	1.11
125	4.8, 3.7	/	2	0.26	45,000	1.08
110	2.4, 1.8	/	2	0.03	20,800	1.13
110	2.4, 1.8	/	4	0.12	43,500	1.13
110	2.4, 1.8	/	6	0.25	62,600	1.09
125	2.4, 1.8	EG	1	0.13	32,700	1.09
125	2.4, 1.8	EG	3	0.38	78,000	1.15
125	2.4, 1.8	EG	4	0.48	94,200	1.15
110	1.2, 0.9	EG	2	0.08	42,600	1.13
110	1.2, 0.9	EG	4	0.20	69,100	1.09
110	1.2, 0.9	EG	8	0.39	92,600	1.08
110	0, 0	/	4	0.07	142,200	1.27
110	0, 0	/	6	0.10	124,100	1.44
110	0, 0	/	10	0.15	121,000	1.30
110	0, 0	EG	2	0.05	226,500	1.59
110	0, 0	EG	8	0.10	176,900	1.63

Experiments were conducted in bulk (/) or ethylene–glycol (EG).

stirring and temperature control (±1 °C) were used throughout the reaction. After the required duration, the reaction was stopped by the cooling of the flask. Excess monomer was evaporated under reduced pressure (0.5 mmHg), and the polymer was recovered as a light-yellow powder after careful drying in a vacuum oven (0.5 mmHg) at 65 °C for 48 h. The absence of residual monomer and the purity of the polymer were checked by ^{1}H NMR in $CDCl_3$: $\delta = 8.27$ (H^6), 7.69–7.76 (H^2), 6.75–6.93 (H^4 and H^5), and 1.48 ppm (main-chain protons).

Measurements

NMR spectra were recorded on a Bruker AC-200P spectrometer. The average molar weights of the polymers were determined by size exclusion chromatography (SEC). Prior to any experiments, the polymers were left to dissolve for 24 h in dimethylformamide (99.5%), which was also used as an eluent (elution rate = 1 mL/min). Before injection, the solutions were filtered through polytetrafluoroethylene (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 (10^3–5×10^6 g/mol). The system had previously been calibrated with standard polystyrenes purchased from Polymer Standard Service. Sample detection was done with a Waters 410 differential refractometer. The results were processed with Millennium software.

RESULTS AND DISCUSSION

The data related with the molar weights and polydispersities of several of the synthesized poly(3-vinylpyridine)s, as characterized by SEC, have been gathered in Table I.

Influence of Nitroxide Concentration

According to Matyjaszewski[7,8] and Fukuda,[12,13] the polymerization rate in the NMRP of styrene is

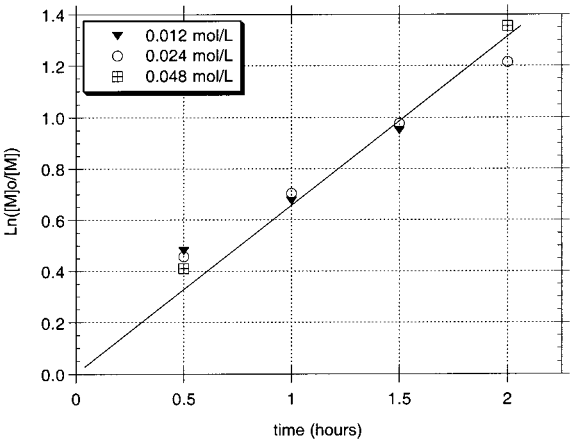


Figure 1. Influence of nitroxide concentration on the bulk polymerization of 3VP at 138 °C in the presence of TEMPO: $\ln([M]_0/[M])$ versus t.

mainly governed by autoinitiation, so nitroxide concentration has no obvious influence on the propagation rate. Similar results are obtained when 3VP is used as a monomer, as shown in Figure 1. Indeed, the $\ln([M]_0/[M])$ values obtained for different nitroxide concentrations are all on the same straight line when plotted as a function of time, $[M]_0$ and $[M]$ standing for the original and current monomer concentrations in the bulk, respectively (as estimated by their proportionality with the weight of formed polymer). Furthermore, the linear evolution of $\ln([M]_0/[M])$ as a function of time proves that the number of active species is almost constant throughout the reaction. Compared with 4VP or even styrene, the kinetics of the reaction is surprisingly fast; this is discussed later.

Controlled polymerization requires a drastic limitation of the number of transfer reactions. The fulfillment of this condition can be evidenced by the plotting of the molar weight of the polymer as a function of conversion. The two straight lines drawn in Figure 2 indicate that transfer is not prevalent. It is remarkable that the final molar weights are directly related to the original TEMPO concentration. The obtained number-average molar weights are particularly high for an NMRP.

As far as polydispersity is concerned, the first seven lines in Table I present very interesting values, which are all the lower as the original TEMPO concentration in bulk is high. In agreement with Matyjaszewski's assumption,[7,8] the slight increase in these polydispersity values when conversion increases can probably be linked to side reactions and particularly to the irreversible decomposition of the terminal C—TEMPO bond, which inevitably occurs throughout the polymerization, reducing the efficiency of TEMPO and, thus, broadening the molar weight distribution. In any case, 3VP tends to yield polymers with very low polydispersity values. This phenomenon is all the more interesting as polydispersities remain low even for macromolecules with high molar weights.

Influence of Temperature

The influence of temperature was studied with experiments conducted at 110, 125, and 138 °C. As reported in Figure 3, a decrease in temperature induces a decrease in the slope of the plot $\ln([M]_0/[M])$ versus time, that is, in the polymerization rate. Moreover, it triggers a longer induction period. Indeed, no induction period is observable for $T = 138$ °C, whereas the plot $\ln([M]_0/[M])$ versus t reveals an induction lag for $T = 125$ °C and even more significantly for $T = 110$ °C. These experimental results enabled us to calculate an overall activation energy of approximately 130 kJ/mol.

As shown in Figure 4, a change in temperature influences the plot of molar weight versus conversion. This is expected because temperature influences the number of radicals that are generated by autoinitiation and, thus, the overall number of active radicals. Because the number of growing polymeric species whose growth must be supplied increases with temperature, the resulting number-average molar weight for the same monomer consumption is reduced at high temperatures: the

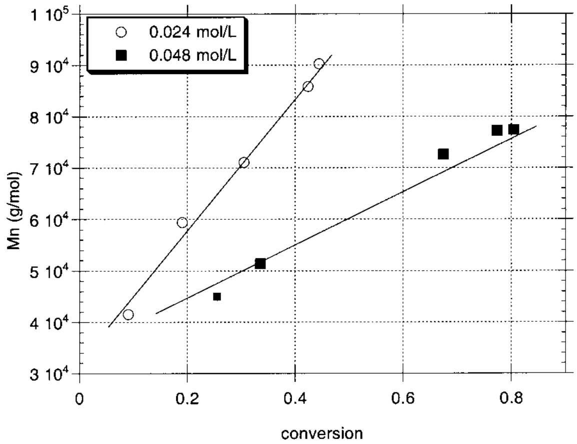


Figure 2. Influence of nitroxide concentration on the bulk polymerization of 3VP at 138 °C in the presence of TEMPO: $\overline{M_n}$ versus conversion.

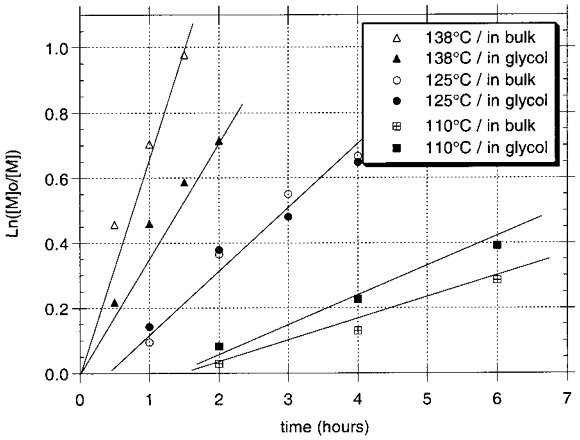


Figure 3. Combined influence of solvent and temperature on the polymerization of 3VP in the presence of TEMPO: ln([M]$_0$/[M]) versus t ([TEMPO]$_0$ = 2.4×10^{-2} mol/L).

same amount of monomer must be shared between a bigger number of growing species. Consequently, plots of $\overline{M_n}$ versus conversion slightly differ from T = 110 °C to T = 125 °C or T = 138 °C. Yet, it is particularly remarkable that all three plots are nevertheless straight lines, even for T = 110 °C, that is, less than 120 °C, which is traditionally regarded as the threshold value for the efficiency of TEMPO. From that perspective, it can be inferred that the polymerization of 3VP is controlled even at temperatures that might appear too low for classical NMRP, which is the first unexpected point to convey the idea that the behavior of 3VP is rather unique compared with the behavior of styrene or even 4VP.

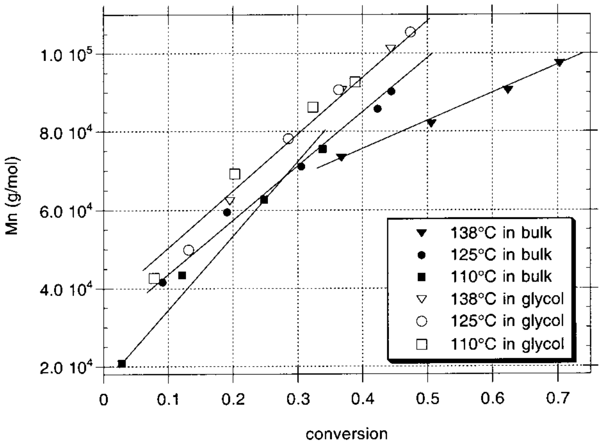


Figure 4. Influence of temperature on the polymerization of 3VP in glycol and in bulk in the presence of TEMPO: $\overline{M_n}$ versus conversion ([TEMPO]$_0$ = 2.4 $\times 10^{-2}$ mol/L).

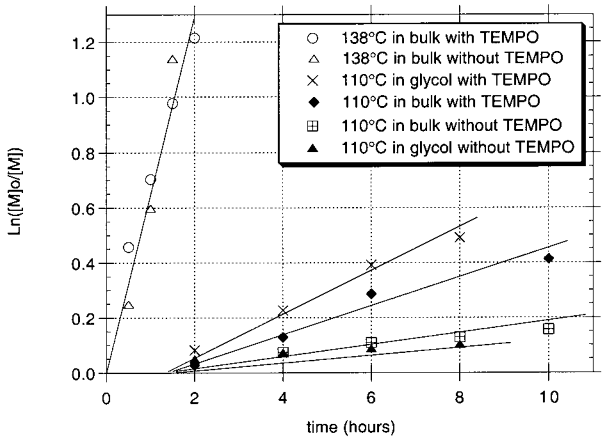


Figure 5. Combined influence of nitroxide and solvent addition on the polymerization of 3VP at different temperatures: ln([M]$_0$/[M]) versus t.

Importance of the Role Played by Nitroxide

To assess the role played by TEMPO in the bulk polymerization of 3VP, it was essential to compare systems with and without initially introduced nitroxide. Be it with or without nitroxide, the effect of temperature is quite logical (Fig. 5): the higher the temperature, the higher the polymerization rate. Thus, the slopes of the corresponding plots of ln([M]$_0$/[M]) versus t are higher at 138 °C than at 110 °C. Yet, although the reaction rate is approximately the same with and without TEMPO at 138 °C, there is a slight difference at 110 °C because, surprisingly, the bulk polymerization of 3VP proceeds more quickly with TEMPO than without TEMPO. This phenomenon is also observed in glycol, as shown in Figure 5. This figure presents further information concerning the effect of ethylene–glycol on the NMRP of 3VP: at 110 °C in the absence of TEMPO, the polymerization rate is logically lower in glycol than in bulk because the presence of a solvent by a dilution effect is supposed to reduce both the radical and monomer concentrations and, consequently, the polymerization rate. Surprisingly, the opposite behavior is observed in the presence of TEMPO, which might suggest that glycol influences the dissociation of the C—TEMPO bond.

Figure 6 is clear-cut evidence that, despite the linear behavior of ln([M]$_0$/[M]) versus t that was observed in Figure 5, the reaction is not controlled in the absence of TEMPO, whether in bulk or in glycol. Indeed, the plot of $\overline{M_n}$ versus conversion is not a straight line, which proves that transfer reactions occur if no nitroxide is provided. This

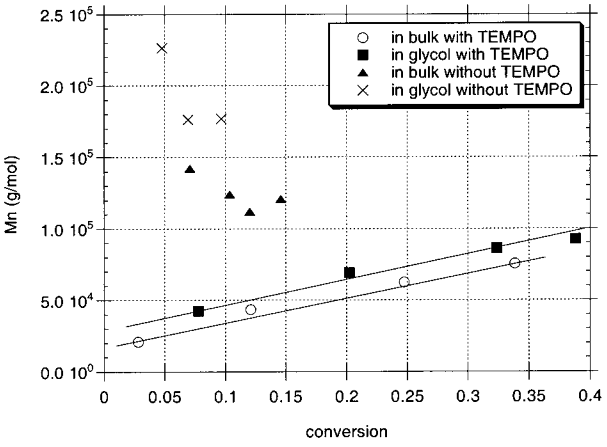


Figure 6. Combined influence of nitroxide and solvent addition on the polymerization of 3VP at 110 °C: $\overline{M_n}$ versus conversion.

statement is all the more surprising because polydispersity remains very low, even for autopolymerization without TEMPO, as reported in Table I. This suggests that the polymerization of 3VP in the absence of additional nitroxide might be governed by a transfer mechanism that could ensure a self-regulation of chain lengths. Unfortunately, we were not in a position to ascertain this hypothesis. In any case, whether with or without TEMPO, the molar weights were higher when the reaction was conducted in glycol. This may be because glycol may trap small radicals issued from the homolytic decomposition of BPO, thus reducing the overall efficiency of the initiator. Another hypothesis is the reaction between some of the TEMPO radicals and ethylene–glycol resulting in a lesser number of chains and, thus, in higher molar weights. This phenomenon would be in agreement with the theory of Georges and others[24,25] concerning the pivotal role of excess nitroxide, whose concentration is said to be reduced by the use of polar additives.[26,27] However, the low polydispersity values that were obtained seem to contradict such an explanation in our very case.

Effect of Solvent When Nitroxide Is Used

Experiments conducted in ethylene–glycol revealed that, compared with its behavior in bulk at the same temperature, the behavior of 3VP polymerized in a solvent that was likely to induce hydrogen bonds with the polymer units was variable. As shown in Figure 3, the reaction is faster in glycol than in bulk at low temperatures (i.e., 110 °C), whereas this trend tends to reverse at high temperatures (i.e., 138 °C) after a transition range (ca. 125 °C) for which the kinetics are almost the same in bulk and in glycol. This changing behavior is probably caused by the opposite influence of temperature on, first, hydrogen bonding that weakens the C—TEMPO bond in the polymeric adduct and, second, the equilibrium between dormant and active species (i.e., polymeric adduct and polymeric radical). Furthermore, contrary to what can be observed in bulk, temperature has no significant influence on the plot of $\overline{M_n}$ versus conversion when the polymerization is conducted in glycol (Fig. 4). Indeed, the values obtained for different temperatures are all on the same line. The effect of glycol as a radical-trapping agent might, here again, be responsible for the reduction of the differences in autopolymerization at different temperatures.

Comparison of 3VP and 4VP

The kinetic behaviors of 3VP and 4VP at 138 °C in the presence of the same amount of TEMPO are quite different. From Figure 7, it can clearly be observed that the polymerization rate of 3VP is much faster than that of its 4-vinyl homologue. It can be suspected that the electronic distribution on the pyridine ring, along with resonance effects, may account for this difference. Indeed, as already mentioned, 3VP presents quite a different polarization of the polymerizable group because there is no conjugating effect between the vinyl group and the C—N bond, contrary to 4VP. Hence, the position of the nitrogen atom is likely

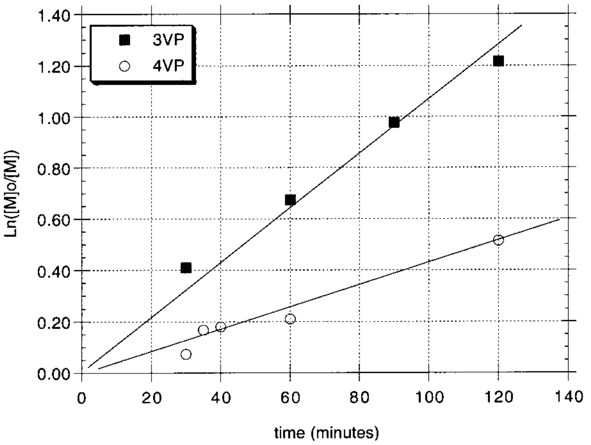


Figure 7. Comparison of 3VP and 4VP involved in bulk polymerizations at 138 °C in the presence of TEMPO ($[\text{TEMPO}]_0 = 2.4 \times 10^{-2}$ mol/L).

to affect the terminal C—TEMPO bond in the polymer and, thus, the characteristics of the reaction itself because the strength of the C—TEMPO bond influences the equilibrium between active and dormant species and, consequently, the way propagation takes place.

CONCLUSION

Compared with styrenic monomers or even 4VP, 3VP appears to be a very interesting monomer in NMRP. Quite long and monodisperse blocks ($\overline{M_n}$ = 99,500 g/mol, $\overline{M_w}/\overline{M_n}$ = 1.22) can be synthesized in bulk within relatively short polymerization times (60 min) because of particularly fast kinetics. According to our experiments, 3VP can be polymerized in a controlled manner with nitroxide, and the influence of temperature and nitroxide concentration is quite logical compared to what is traditionally observed in the field of NMRP. 3VP is also to be considered a very atypical monomer, yielding low-polydispersity macromolecules even when the reaction is conducted below 120 °C or without additional TEMPO (although, in the latter case, the reaction is not controlled in regard to the evolution of the number-average molar weight as a function of conversion). Experiments conducted in a protic solvent (i.e., ethylene–glycol) revealed that it was also possible to rapidly obtain quite monodisperse species by solution polymerization, which is a major perspective for monomers that are not polymerizable in bulk. Moreover, the difference between bulk and solution polymerizations was proven to be temperature-dependent. Further experiments are bound to investigate the way ethylene–glycol influences the C—TEMPO bond dissociation.

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