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Living Anionic Homopolymerization and Block Copolymerization of 4-Vinylpyridine at "Elevated" Temperature and Its Characterization by Size Exclusion Chromatography

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ABSTRACT: The anionic polymerization of 4-vinylpyridine (4VP) has been investigated in 9/1 pyridine/THF at 0 °C. After characterization of the living character of 4VP polymerization, its copolymerization with *tert*-butyl methacrylate (tBMA) has been carried out also successfully. Their relative reactivity ratios have been determined. Solvent composition as well as temperature have been varied in order to evaluate their influence on the final molecular characteristics of the polymers. Finally, a new SEC methodology in 8/1/1 *N*,*N*-dimethylformamide/triethylamine/pyridine has been developed.

Introduction

Since the pioneering work of Szwarc,[1] anionic polymerization has been thoroughly developed. This living process has proved to be a highly versatile methodology to synthesize polymers with controlled molecular weight and molecular weight distribution (MWD). In contrast to poly(2-vinylpyridine), which has already been anionically synthesized in the early 1960s,[2] anionic poly(4-vinylpyridine) has been scarcely studied until recently,[3,4] despite its more efficient properties due to the higher accessibility of the nitrogen, i.e. easier quaternization to afford polyelectrolytes.[5] Indeed, its later development is partly related to its insolubility above a certain molecular weight in THF, the most common solvent for anionic polymerization.

Very recently, two approaches have been proposed. Varshney et al.[3] have used THF added with *N*,*N*-dimethylformamide to ensure solubility during the polymerization process. A living character was observed when using diphenylmethylpotassium as initiator at −78 °C and a 2 wt % polymer concentration. Nevertheless, two polymer species were observed when the polymerization was carried out at 0 °C. The major fraction close to the theoretical molecular weight shows a broad molecular weight distribution (1.60). Moreover, a second minor fraction at much higher molecular weight has been observed, which should find its origin in side reactions.

Nugay et al.[4] have chosen pyridine as an additive to THF to ensure solubility in the medium. They observed complete conversion as well as some copolymerization with dimethylsiloxane at −78 °C. Nevertheless, no SEC characterization has been carried out. Moreover, they assumed that block copolymerization going from 4VP to dimethylsiloxane was successful on the sole basis that after quaternization, the resulting polymer was soluble in water, a nonsolvent for PDMS. Only SEC measurements would allow us to determine if the block copolymer is not contaminated with the first sequence, P4VP. Indeed, even if contaminated by homopoly (4VP), the final product would also afford a complete water solubility upon quaternization.

The homo- and copolymerization of 4VP at 0 °C will be described in this paper. Their living character will be demonstrated as well as the influence of the solvent nature on the polymerization control. An efficient SEC analysis will also be developed.

Experimental Section

4-Vinylpyridine and *tert*-butyl methacrylate were first vacuum distilled from calcium hydride and then stored under a nitrogen atmosphere at −20 °C. Before polymerization, 4VP and tBMA were diluted once with toluene, treated with 1 M triethylaluminum in toluene until a yellowish green color appeared, and finally redistilled under reduced pressure just prior to polymerization.

Diphenylmethyllithium was prepared at room temperature by reacting diphenylmethane with lithium naphthalenide prepared from lithium and naphthalene in THF at room temperature. Diphenylhexyllithium was prepared at room temperature by reacting 1,1-diphenylethylene with *n*-butyllithium in toluene.

Lithium chloride was flame dried under vacuum just prior to polymerization and stored under nitrogen. THF was

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Table 1. Anionic Homo- and Copolymerization of 4VP Initiated by Diphenylmethyllithium in a Pyridine/THF Mixture

	poly(4VP)				poly(4VP-*b*-tBMA)					
	M_n				M_n					
expt	theor	SEC	M_w/M_n	f^a	theor	SEC	NMR[b]	M_w/M_n	f^c	composition[d]
1[e]	7400	8400	1.1	0.88						
2[e]	9800	11000	1.06	0.89	28 000	15 800	32 300	1.1	0.87	34−66
3[f]	4900	5700	1.24	0.86	14 000	10 500	15 800	1.18	0.88	36−64

[a] $f = M_n$(theor)/M_n(SEC). [b] M_n(NMR) = M_n(SEC) of the first block divided by the weight percentage of this block as measured by NMR. [c] $f = M_n$(theor)/M_n(NMR). [d] Weight composition measured by NMR. [e] −78 °C; in 60/40 (v/v) pyridine/THF; total monomer concentration = 5 wt %. [f] 0 °C; in nondistilled 90/10 (v/v) pyridine/THF; total monomer concentration = 16 wt %.

purified by refluxing over a freshly prepared sodium−benzophenone complex. Pyridine was purified by distillation over *sec*-butyllithium.

Polymerization was carried out under dry nitrogen in flasks equipped with three-way stopcocks. All glassware was flamed under vacuum before use. Solutions were transferred through stainless steel capillaries or with glass syringes, through a rubber septum.

The solvent cooled at the required temperature (−78, −45, 0, or 25 °C) was dropwise added with diphenylmethyllithium until a persistent yellow color was observed. The required amount of this initiator was then transferred to the medium, followed by the purified monomer. In the case of homopolymers, the polymerization was quenched by adding degassed methanol. In the case of copolymerization, an aliquot was withdrawn for characterization and the second monomer was then injected. The copolymerization was finally quenched also with degassed methanol. The polymer was recovered by complete solvent removal.

Characterization. Size exclusion chromatography (SEC) was carried out in *N*,*N*-dimethylformamide added with 10% triethylamine and 10% pyridine at 45 °C using a Hewlett-Packard 1050 liquid chromatograph equipped with a mixed C PLGel column and a Hewlett-Packard 1047A refractive index detector. Poly(2-vinylpyridine) standards were used for calibration. ^{1}H spectra were recorded at 400 MHz with Brüker AM 400 superconducting magnet equipment.

Results and Discussion

Homo- and Copolymerization at 0 °C in 9/1 Pyridine/THF. Despite the extended potential applications of P4VP, astonishingly, its anionic polymerization in a well-controlled living process has scarcely been reported mainly due to its insolubility in THF, a common solvent for anionic polymerization. Insolubility in THF also restricts polymer characterization by SEC: a new SEC method had then to be developed. *N*,*N*-Dimethylformamide, a good solvent for P4VP, which has been shown to be efficient for poly(2-vinylpyridine)[6] SEC characterization, has been used as eluent. Unfortunately, it is unable to avoid P4VP adsorption on the column, highlighting the higher nitrogen accessibility compared to 2VP. Therefore, a few percent triethylamine, which has been shown to be efficient to avoid polymer adsorption with (dimethylamino)ethyl methacrylate[7] and 2-vinylpyridine[6] in THF, has been added to the eluent. Once again, no signal has been observed. Since an additive has the purpose of coating adsorption sites with a small molecule comparable to the anchoring group of the polymer, triethylamine has then been replaced by pyridine, better mimicking the polymer. Unfortunately, adsorption could not be avoided either. But very surprisingly, if triethylamine and pyridine are combined and added to the eluent, no significant adsorption is observed anymore. A 10/10/80 volume % triethylamine/pyridine/*N*,*N*-dimethylformamide eluent has thus been used to characterize the polymers reported in the present paper. Contrarily to Varshney et al., poly(2-vinylpyridine) and not polystyrene standards have been used for calibration. The latter has been disregarded, since some retention of polystyrene standards was observed in polar solvents such as *N*,*N*-dimethylformamide as well as *N*-methylpyrrolidone.[8] Moreover, P2VP calibration is believed to better match 4VP molecular weight determination.

Table 2. Anionic Homopolymerization of 4VP at 0 °C in 90/10 Pyridine/THF vol% (0.48 mol/L 4VP; Initiator, Diphenylmethyllithium)

expt	M_n(theor)	M_n(SEC)	f^a	M_w/M_n
4	4 300	5 600	0.77	1.15
5	6 700	8 000	0.84	1.15
6	8 700	10 700	0.81	1.15
7	12 800	15 600	0.82	1.15
8	15 800	19 100	0.83	1.1
9	21 400	24 500	0.87	1.1
10	54 400	58 300	0.93	1.1
11[b]	9 300	19 500	0.48	1.3

[a] The initiation efficiency is M_n(theor)/M_n(SEC). [b] The initiator is *sec*-butyllithium.

In a first approach, 4VP has been polymerized in 60/40 vol % pyridine/THF at −78 °C. At this temperature, a higher amount of pyridine leads to freezing of the solvent. Diphenylmethyllithium has been used as initiator in the presence of lithium chloride. The latter has been shown previously to afford narrow MWD with methacrylates[9,10] as well as 4VP[3] and 2VP.[11] A narrow MWD as well as a good agreement between the observed and theoretical molecular weights have been obtained (Table 1; experiment 1). Even more, its sequential block copolymerization with *tert*-butyl methacrylate has also been successful (Table 1; experiment 2). In view of these promising results, a general approach may be envisioned. Unfortunately, if much higher molecular weights are desired, the pyridine percentage has to be raised in order to avoid insolubility. As mentioned previously, 60 vol % pyridine is close to the maximum allowed before freezing of the medium. Therefore, if one is concerned with higher molecular weight, a higher temperature should be used in order to allow an increase in pyridine content. Various temperatures as well as solvent mixture compositions have been evaluated: the polymerization at 0 °C in 90/10 vol % pyridine/THF, which affords the best compromise, will be described first, and the other conditions, in the subsequent section.

Anionic polymerization of 4VP has thus been carried out in 90/10 vol % pyridine/THF at 0 °C. Diphenylmethyllithium was used as initiator, and the polymer concentration was kept at 5 wt %, twice the concentration reported by Varshney et al. Narrow MWD as well as a good agreement between theoretical and the observed molecular weights have been observed (Table 2 and Figure 1). Moreover, if a second feed is added, an increase of molecular weight in agreement with the feed weight is observed without any noticeable broadening of the MWD. In an example, M_n(SEC) = 8000 has

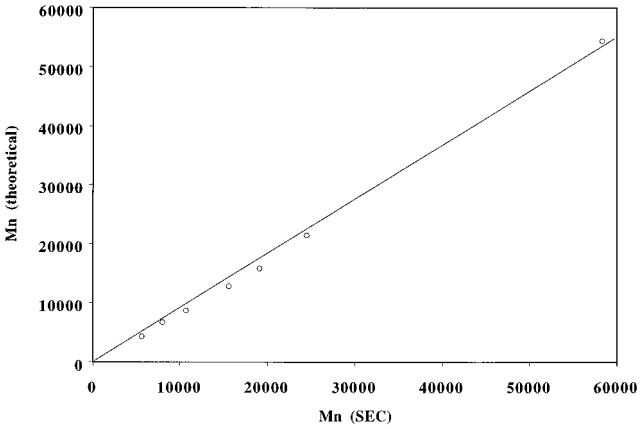


Figure 1. Anionic polymerization of 4VP in 90/10 pyridine/THF vol % at 0 °C.

been observed upon polymerization of the first feed, with an initiation efficiency (f) of 0.84 and a narrow MWD ($M_w/M_n = 1.15$). The complete conversion of a second monomer feed has resulted in a polymer of M_n(SEC) = 15 600, while keeping constant both f and M_w/M_n. If one considers the usual temperature for anionic polymerizations, ca. −78 °C, these results are very promising. Moreover, *sec*-butyllithium has also been used as initiator instead of diphenylmethyllithium. A slightly broader MWD (1.3) as well as a poorer initiator efficiency (0.48) have been observed (Table 2; experiment 11). Nevertheless, if one considers these extreme conditions compared to classical anionic polymerization, these results are unexpectedly good.

The 4VP living character being established, its block copolymerization with tBMA has been carried out under the same conditions. Thus, the 4VP polymerization has been initiated by diphenylmethyllithium at 0 °C in a pyridine/THF mixture (90/10 v/v). These living poly(4VP) chains (M_n(SEC) = 3300; $M_w/M_n = 1.15$ and f = 0.94) have successfully initiated tBMA with formation of a block copolymer of a 24-76 wt % composition and an unchanged polydispersity. The final M_n (13 700), as measured by ^{1}H NMR, is close to the expected value (13 200), which results in $f = 0.96$ for the block copolymerization.

In order to highlight the versatility of the method, 4VP has been block copolymerized with tBMA in nondistilled solvents at a concentration of 16 wt %. The mixed solvent has just been degassed and dried in situ by addition of diphenylmethyllithium until a permanent yellow coloration appears. Then the required catalyst amount has been added and the copolymerization allowed to proceed at 0 °C. Even in these conditions, a good control is observed (Table 1; experiment 3).

Finally, the temperature has been raised to room temperature and the 4VP polymerization initiated by diphenylmethyllithium in 90/10 vol % pyridine/THF. A quite narrow molecular weight distribution has been observed (1.2) as well as a 0.88 initiator efficiency. Moreover when a second feed of 4VP is added, e.g. to a polymer of a 12 700 M_n, an increase in molecular weight is observed (up to 26 000) in agreement with the total feed, while keeping the initiator efficiency and polydispersity unchanged. So a living character can also be reached even at room temperature. Block copolymerization with tBMA has also been successful at room temperature, since the initiation of the tBMA polymerization by "living" poly(4VP) chains (M_n = 4800; f = 0.83 and $M_w/M_n = 1.15$) has resulted in a poly(4VP-*b*-tBMA) of a 25−75 wt % composition (M_n = 19 200; f = 0.81 and $M_w/M_n = 1.15$). Nevertheless, these conditions are much more sensitive to any noxious impurities and required therefore very careful precautions. On a laboratory scale, 0 °C should be preferred to allow good

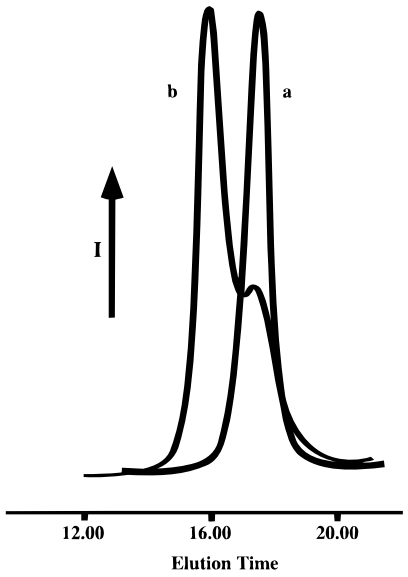


Figure 2. Anionic block copolymerization of tBMA with 4VP in 90/10 pyridine/THF vol % at 0 °C initiated by diphenylmethyllithium (PMMA standards): (a) poly(tBMA), M_n(SEC) = 5800, $M_w/M_n = 1.08$; (b) poly(tBMA-*b*-4VP), M_n(SEC) = 11 900, $M_w/M_n = 1.44$. Composition (wt %): 75−25.

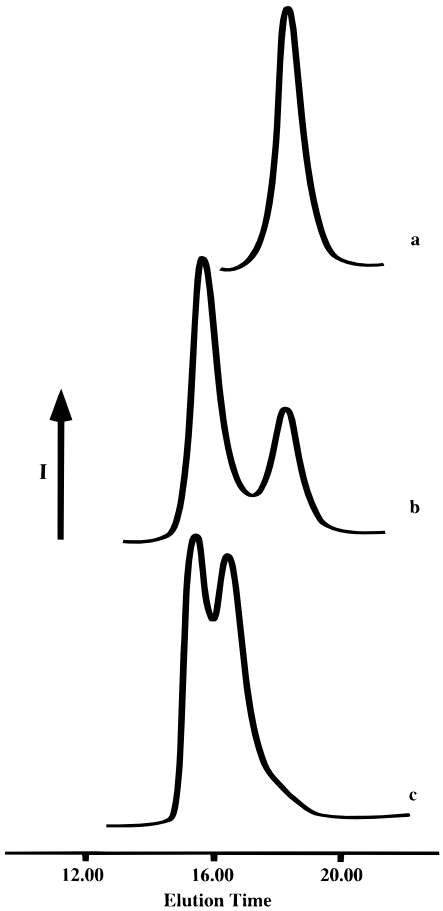


Figure 3. Anionic synthesis of poly(tBMA-*b*-4VP-*b*-tBMA) in THF at 0 °C initiated by diphenylmethyllithium (PMMA standards): (a) poly(tBMA), M_n(SEC) = 5000, $M_w/M_n = 1.14$; (b) poly(tBMA-*b*-4VP), M_n(SEC) = 10 600, $M_w/M_n = 2.3$; (c) poly(tBMA-*b*-4VP-*b*-tBMA), M_n(SEC) = 18 600 $M_w/M_n = 1.55$.

control without any stringent purification procedure.

The reverse copolymerization of tBMA and 4VP has then been attempted in order to evaluate their relative reactivity at 0 °C in 9/1 pyridine/THF. Despite complete conversion, some contamination of the final copolymer by homopoly(*tert*-butyl methacrylate) has been observed (Figure 2). Either some side reactions could be at the origin of this contamination or the initiation of 4VP by living poly(tBMA) anions is too slow compared to the propagation rate of 4VP. In the latter hypothesis, all the 4VP units would be consumed before complete initiation by the living poly(tBMA) anions, giving rise to a mixture of living diblock and homopoly(tBMA) chains: this second hypothesis is believed to better reflect the reality.

In order to evaluate that hypothesis, the copolymerization has been repeated in pure THF at 0 °C. Indeed, since 4VP polymerization is initiated by living homopoly(tBMA) chains, no insolubility of the diblock should be observed, as long as the diblock copolymer is not too rich in 4VP. The interest to repeat the polymerization in THF relies upon the fact that much more contamination is observed under these conditions, and so detection of this phenomenon by SEC is easier. After removal of an aliquot for characterization, a fresh feed of tBMA has been added to the polymerization medium. If the contaminant of the diblock copolymer is living homopoly(tBMA), the complete distribution curve should be shifted to higher molecular weights. The final product exhibits such a shift (Figure 3). This would then mean that 4VP reactivity, although lower than the tBMA one, is close enough to allow its slow initiation by homopoly(tBMA). In contrast, if the copolymerization is repeated under the same conditions with 2VP instead of 4VP, no reinitiation is observed. The reverse copolymerization will be developed in more details in a forthcoming paper.

In view of the discrepancy encountered with the reverse sequential copolymerization, polymerization of tBMA/4VP mixtures has been considered at 0 °C in 9/1 pyridine/THF to determine the reactivity ratios. Very surprisingly, despite the contamination observed for the sequential copolymerization, the copolymers obtained by polymerizing simultaneously the two comonomers exhibit a quite narrow MWD ($M_w/M_n = 1.2$). This result is again in disfavor of some potential side reactions envisioned above.

The extended Kelen−Tüdös method has been used to estimate the relative reactivity ratios of tBMA and 4VP. The copolymer composition has been determined by comparing the pyridinyl ring peaks to the *tert*-butyl peak at 1.44 ppm (tBMA). The extended Kelen−Tüdös method is expressed by the following equations:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$$

where

$$\eta = G/(\alpha + F) \quad \text{and} \quad \xi = F/(\alpha + F)$$

$$\alpha = (F_{min}F_{max})^{1/2}$$

$$F = Y/Z^2 \quad \text{and} \quad G = (Y - 1)/Z$$

$$Z = \log(1 - \zeta_1)/\log(1 - \zeta_2)$$

and

$$\zeta_2 = w(\mu + X)/(\mu + Y)$$

$$\zeta_1 = \zeta_2(Y/X)$$

in which X and Y represent the molar ratios of monomer 1 to monomer 2 in the comonomer feed and the resulting copolymer, respectively. W corresponds to the weight conversion of the copolymerization, and μ is the molecular weight ratio of monomer 2 to that of monomer 1.

The copolymerization data have been plotted in Figure 4 according to the extended Kelen−Tüdös equation. The intercepts at $\xi = 0$ and $\xi = 1$ of the ξ versus η plot give as an estimation $r_{tBMA} = 13.3 \pm 6.6$ and $r_{4VP} = 0.47 \pm 0.3$. This confirms the higher reactivity of tBMA compared to 4VP. The copolymer could then be depicted as a "tapered diblock" copolymer, composed of a mixed sequence constituted of poly(tBMA) increasingly contaminated by 4VP, and progressively followed by a poly4VP sequence formed after complete consumption of tBMA monomer.

Homopolymerization under Various Conditions. The influence of solvent composition as well as temperature on the molecular characteristics has also been studied. 4VP polymerization has been studied first at −45 °C, which is the temperature used by Huynh-Ba et al.[12] for the living anionic polymerization of methacrylates in pure pyridine. When no THF was added to the solvent, diphenylhexyllithium, prepared in toluene, was used as initiator instead of diphenylmethyllithium, the latter being prepared in THF. 4VP homopolymerization has been first carried out in pure pyridine. A very narrow MWD has been observed as well as an initiator efficiency factor of 0.75 (Table 3; experiment 12). If 10% THF is added to pyridine, a narrow molecular weight distribution is also observed, and the initiator efficiency is then improved: 0.87 (Table 3; experiment 13). If, instead of THF, a 10-fold molar excess of lithium chloride compared to the initiator is added to pyridine, a still narrower MWD is observed as well as a better initiator efficiency (Table 3; experiment 14). Lithium chloride has been shown previously to improve the control of (meth)acrylates,[9,10] 2-vinylpyridine,[11] and 4-vinylpyridine.[3] As shown by Huynh-Ba et al. with methacrylates, the polymerization is thought to occur via an equilibrium between a σ-complex and free anions (Scheme 1). The solvent composition and the temperature influence the exchange rate between the two species and their relative proportions. So pyridine would act as the propagating species and not just as the solvent. This would explain the absence of any noticeable side reactions on the 4VP ring, contrarily to previous reports at such high temperatures.[2b,13] The exact influence of either THF or lithium chloride as a function of temperature is not yet well established and will be studied in the future.

Anionic polymerization of 4VP has then been studied at 0 °C. In pure pyridine, a narrow MWD has been obtained with an initiator efficiency of 0.9 (Table 3; experiment 15). In the presence of 10 vol % THF (Table 2) or of LiCl (Table 3; experiment 16), a comparable MWD and initiator efficiency are also observed within experimental errors. Remarkably enough, all three conditions afford comparable results with an initiator efficiency quite close to the one observed at −45 °C, despite the quite high temperature. Although the three methods yield the same results, addition of THF has been preferred to the use of pure pyridine or lithium chloride. The former has been disregarded since the pyridine content should be lowered as much as possible due its nasty smell and its potential toxicity, and its

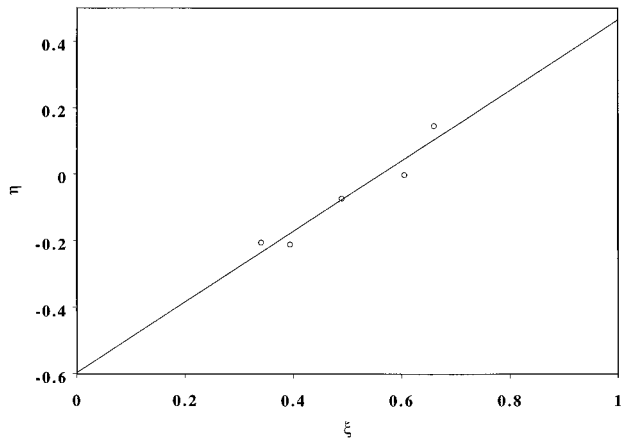


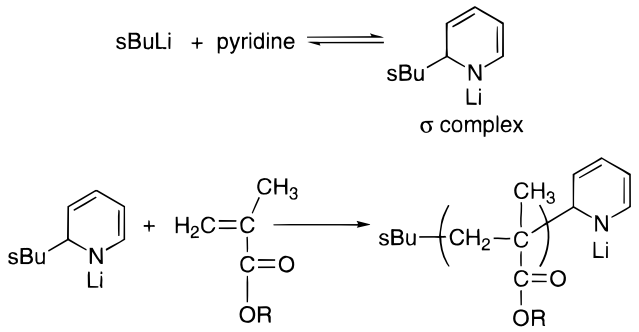
Figure 4. Extended Kelen−Tüdös plot $\eta = (r_{4VP} + r_{tBMA}/\alpha)\xi - r_{tBMA}/\alpha$.

Table 3. Anionic Homopolymerization of 4VP in Pyridine (0.48 mol/L 4VP)

expt	additive	M_n(theor)	M_n(SEC)	f	M_w/M_n
12[a]		10 000	13 400	0.75	1.08
13[a]	THF	11 700	13 500	0.87	1.08
14[a]	LiCl	11 000	11 500	0.96	1.05
15[b]		9 200	10 200	0.9	1.15
16[b]	LiCl	15 500	18 000	0.86	1.13
17[c]		11 500	17 900	0.64	1.2
18[c]	THF	11 300	12 700	0.89	1.2
19[c]	LiCl	14 700	16 500	0.89	1.22

[a] −45 °C. [b] 0 °C. [c] Room temperature.

Scheme 1



content reduction should be inversely proportional to the desired molecular weight in order to keep solubility. Nevertheless, this reduction should be limited since pyridine is acting more than just as a solvent. Lithium chloride has also been disregarded since reproducibility of its complete drying is not so straightforward, especially if one envisions production on a larger scale.

For practical purposes, room temperature has finally been considered (Table 3; experiments 17−19). In pure pyridine, a narrow molecular weight has still been observed (1.2) but with a poorer initiator efficiency (0.64). THF addition improves the initiator efficiency with a comparable MWD, and if THF is replaced by lithium chloride, comparable molecular parameters are obtained.

Conclusion

The living homopolymerization of 4VP has been demonstrated in 9/1 pyridine/THF at 0 °C. Well-defined, i.e. in terms of molecular weight and MWD, homo- and copolymers can thus be synthesized at this quite high temperature (and even at room temperature in some cases). The influence of solvent composition as well as temperature has been reported and indicates the key role played by pyridine to control 4VP polymerization without side reactions on the 4VP ring. The initiation of 4VP polymerization by living poly(tBMA) chains has been shown not to be straightforward due to the relative reactivity ratios of the two monomers. This copolymerization can be controlled by choosing the correct solvent mixture, as will be exemplified in a forthcoming paper. This highlights again the crucial role displayed by the solvent. Finally, a new SEC method has been developed in 8/1/1 *N*,*N*-dimethylformamide/triethylamine/pyridine. The hydrolysis of the *tert*-butyl ester of the poly(4VP-*b*-tBMA) copolymers is an easy way toward water soluble amphiphilic block copolymers, whose synthesis and properties will be reported in a subsequent paper.

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