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Anionic Block Copolymerization of 4-Vinylpyridine and *tert*-Butyl Methacrylate at "Elevated" Temperatures: Influence of Various Additives on the Molecular Parameters

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ABSTRACT: The living anionic polymerization of 4-vinylpyridine (4VP) in 9/1 pyridine/THF at 0 °C has been reported lately (Creutz, S.; Teyssié, Ph.; Jérôme, R. *Macromolecules* **1997**, *30*, 1). The success of its block copolymerization with *tert*-butyl methacrylate (tBMA) has been shown to be dependent on the addition mode, highlighting the difference in reactivity between the two monomers. Moreover, the (co)solvent also strongly influences the fate of that copolymerization. Thus, the impact of various (co)solvents and additives has been investigated more thoroughly, revealing the interesting possibility of modifying the apparent relative reactivities of these two monomers.

In contrast to 2-vinylpyridine, which has already been anionically polymerized in the early 1960s,[2] 4-vinylpyridine (4VP) anionic polymerization has been scarcely studied until recently,[3,4] despite its more interesting properties due to the higher accessibility of the nitrogen atom, i.e., easier quaternization to afford polyelectrolytes,[5] etc. In fact, that slower development is partly related to the polymer insolubility above a certain molecular weight in THF, the most common solvent for anionic polymerization.

Very recently, we have shown that the homopolymerization of 4VP at 0 °C in 9/1 pyridine/THF could be achieved in a perfectly living manner.[1] Moreover, the temperature could be raised to room temperature even without significant loss of control on the molecular parameters. 4VP block copolymerization with tBMA was also performed in a controlled manner, provided that the copolymerization is started with 4VP with subsequent addition of tBMA. The reverse mode of addition was then investigated. At first, we thought that pyridine was no longer required, since the solubility of P4VP might be ensured during polymerization by the living PtBMA chains within the limits of a moderate content in 4VP. Unfortunately, when 4VP polymerization was initiated by living PtBMA lithium anions in THF at 0 °C, the final product was strongly contaminated by homo-PtBMA. In contrast, addition of 90 vol % pyridine to THF at 0 °C reduced the contamination to a minor amount. Finally, the "contaminant" was observed to be still living, since both the diblock copolymer and contaminant moved to higher molecular weights upon addition of a second feed of tBMA in THF at 0 °C. A deeper investigation on this copolymerization will be the subject of the present publication.

Experimental Section

Purification of 4VP, tBMA, pyridine, THF, and LiCl and the polymerization procedure were detailed elsewhere.[1] (Diphenylmethyl)lithium, -sodium, and -potassium were prepared at room temperature by reacting diphenylmethane with lithium, sodium, and potassium naphthalenide prepared in THF at room temperature from lithium, sodium, and potassium and naphthalene, respectively.

Hexamethylphosphoric triamide (HMPA), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), diisopropylamine (DiPA), and *N*-methyl-2-pyrrolidinone (NMP) were dried over calcium hydride. Lithium *tert*-butoxide was prepared in situ by reacting *tert*-butanol with (diphenylmethyl)lithium.

THF containing the required additive at the desired temperature (−45 °C, 0 °C or 25 °C) was added dropwise with (diphenylmethyl)lithium, -sodium, or -potassium until a persistent yellow color was observed; the required amount of this initiator was then transferred to the medium, followed by the purified tBMA. After polymerization, an aliquot was withdrawn for characterization and 4VP was then injected. The copolymerization was finally quenched with degassed methanol. The polymer was recovered by complete solvent removal. As an alternative, the last copolymerizations were carried out in pure THF. The specified additive (DMF, DiPA, or $AlEt_3$) was mixed with the purified 4VP monomer prior to addition of this mixture to the reaction medium. Complete conversions were obtained.

Characterization. Size exclusion chromatography (SEC) was carried out at 45 °C in a mixture of 80% DMF, 10% triethylamine, and 10% pyridine using a Hewlett-Packard 1050 liquid chromatograph equipped with a mixed C PLGel column and a Hewlett-Packard 1047A refractive index detector. Since poly(methyl methacrylate) standards were used for calibration, apparent molecular weights were made available and reported in the legends of the figures. The composition of the block copolymers was determined by ^1H NMR (see legends of figures), and the spectra were recorded at 400 MHz with Brüker AN 400 superconducting magnet equipment. Since the comonomer conversion was close to completion, the theoretical and experimental compositions of the copolymers recovered by solvent removal were in good agreement.

Results and Discussion

Despite the extended potential applications of P4VP, the anionic polymerization of 4VP in a well-controlled living process has scarcely been reported, mainly due to the polymer insolubility in THF, a common solvent for anionic polymerization. Addition of pyridine, a solvent for P4VP, has recently been shown to allow the living homopolymerization up to room temperature.[1] Under these conditions, living P4VP chains initiate tBMA with formation of diblock copolymers in a well-controlled manner. A further improvement would thus be to carry out the copolymerization in the absence of pyridine. In this respect, the block copolymerization in the reverse mode was expected to be the right answer, since the solubility would be imparted by the PtBMA first block during the polymerization process. However, as mentioned above, the final product exhibits a strong contamination due to the first sequence, which was,

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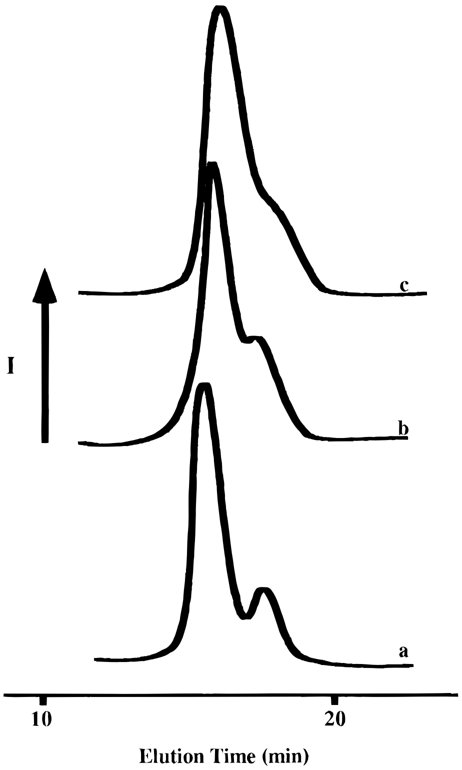


Figure 1. Anionic polymerization of poly(tBMA-*b*-4VP) in 9/1 vol/vol pyridine/THF initiated by (diphenylmethyl)lithium. (a) At −45 °C: M_n(tBMA) = 6700 (M_w/M_n = 1.06); M_n (tBMA-*b*-4VP) = 20 200 (M_w/M_n = 1.6); composition (wt %), 66−34. (b) At 0 °C: M_n (tBMA) = 5800 (M_w/M_n = 1.08); M_n(tBMA-*b*-4VP) = 11 900 (M_w/M_n = 1.44); composition (wt %), 75−25. (c) At 25 °C: M_n(tBMA) = 4800 (M_w/M_n = 1.2); M_n(tBMA-*b*-4VP) = 12 400 (M_w/M_n = 1.6); composition (wt %), 71−29.

however, strongly reduced when the reaction was conducted in a 9/1 (v/v) pyridine/THF mixture. At first, side reactions were suspected. However, if a fresh feed of tBMA is added to the "contaminated" diblock, the complete molecular weight distribution moves to higher molecular weights. An explanation based on side reactions is thus already quite dubious. Moreover, in the case of side reactions, an increase in temperature should be unfavorable to the copolymer formation and vice versa. Accordingly, the block copolymerization has been carried out at −45, 0, and at +25 °C, respectively, in a 9/1 pyridine/THF mixture (the best performing solvent for 4VP homopolymerization). Surprisingly, at −45 °C (Figure 1a), there is an increase in the homo-PtBMA contamination compared to what happens at 0 °C (Figure 1b). In contrast, the contamination degree at 25 °C (Figure 1c) is comparable to that observed at 0 °C. The hypothesis of side reactions is thus even more questionable.

Very recently,[1] we have also reported the reactivity ratios of tBMA/4VP ($r_{tBMA} = 13.3 \pm 6.6$ and $r_{4VP} = 0.47 \pm 0.3$) in 9/1 pyridine/THF at 0 °C, which highlights the much higher reactivity of tBMA compared to 4VP. Since the two comonomers and related anions are of such different reactivities, crosspolymerization from tBMA to 4VP is very unfavorable, and potentially compatible with an improvement at 0 and 25 °C compared to −45 °C. Another kinetic aspect of this crosspolymerization also has to be taken into account. If the crossover rate constant from tBMA to 4VP is smaller than the 4VP propagation rate constant, part of the PtBMA chains might not have the opportunity to add 4VP before complete 4VP conversion. This must accordingly lead to a bimodal molecular weight distribution, i.e., block copolymer and homo-PtBMA, which are both living and able to initiate the polymerization of a fresh feed, as exemplified above. Thus, any significant change in the crosspolymerization rate constant/4VP propagation rate constant ratio should modify the degree of contamination of the block copolymer by homo-PtBMA. So it may be proposed that in pyridine (ϵ = 12.3) the crosspolymerization reaction would be faster than in THF (ϵ = 7.5), due to a higher dielectric constant. In other words, the reactivity of the tBMA anions toward the 4VP monomer would be increased. We should then observe a smoother crosspolymerization since we have favorably modified the relative energy level between 4VP and living PtBMA anions. However, we also have to make the hypothesis that 4VP propagation is influenced to a lesser extent.

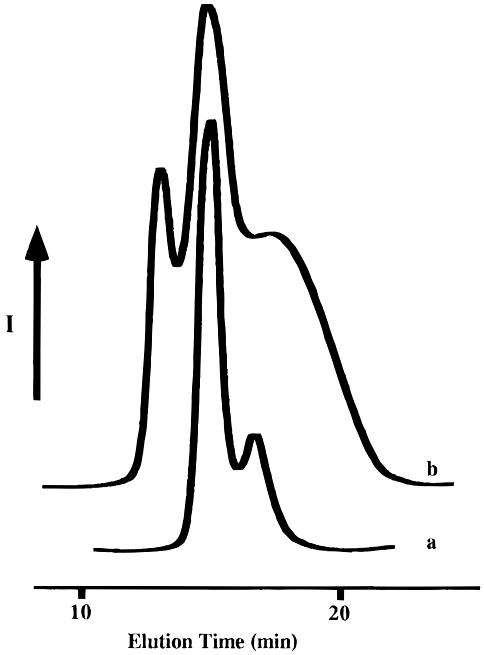


Figure 2. Anionic polymerization of poly(tBMA-*b*-4VP) in THF initiated by (diphenylmethyl)potassium. (a) At 0 °C: M_n(tBMA) = 10 600 (M_w/M_n = 1.2); M_n(tBMA-*b*-4VP) = 31 600 (M_w/M_n = 1.6); composition (wt %), 70−30. (b) At 25 °C: M_n(tBMA) = 4400 (M_w/M_n = 1.8); M_n(tBMA-*b*-4VP) = 14 600 (M_w/M_n = 10.7); composition (wt %), 70−30.

Role of Ion-Pair Structure and Complexation. The relative reactivities of the anions and the propagation rate, which are the two keys controlling the crosspolymerization, may be tuned by additives such as lithium *tert*-butoxide[6] (4-fold molar concentration of the initiator) or lithium chloride[7] (10-fold molar concentration of the initiator). The copolymerization has then been repeated in THF at 0 °C in the presence of one of these additives. Although the former improves the crosspolymerization, contamination persists. In contrast, the latter worsens the situation. When lithium *tert*-butoxide is used as a ligand, Janata et al.[8] have shown that the *tert*-butyl acrylate anions (tBA) are stabilized. If it is so for the living PtBMA chains, the crosspolymerization rate should be decreased, which is not the desired effect. Nevertheless, this ligand also drastically reduces the propagation rate of tBA (by a factor of 200). Moreover, Hogen-Esch et al.[9] have shown that lithium *tert*-butoxide in toluene at −78 °C has a strong effect on the tacticity of poly(2-vinylpyridine), due to a strong coordination to the living chain end. Thus, within the limits of this analogy accuracy, the 4VP

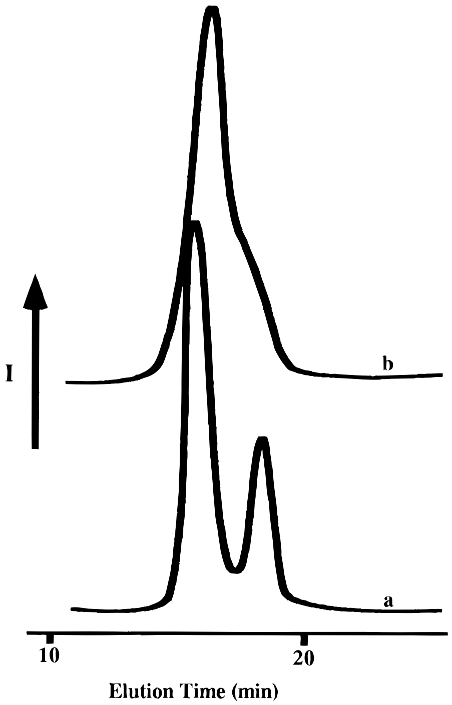


Figure 3. Anionic polymerization of poly(tBMA-*b*-4VP) at 0 °C initiated by (diphenylmethyl)lithium. (a) In 99/1 vol/vol THF/pyridine: M_n(tBMA) = 4900 (M_w/M_n = 1.08); M_n (tBMA-*b*-4VP) = 11 000 (M_w/M_n = 2); composition (wt %), 73−27. (b) In pyridine: M_n(tBMA) = 6400 (M_w/M_n = 1.13); M_n(tBMA-*b*-4VP) = 13 600 (M_w/M_n = 1.6); composition (wt %), 74−26.

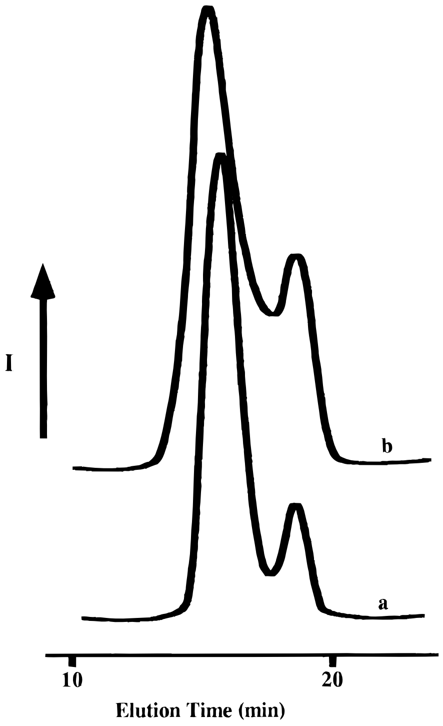


Figure 4. Anionic polymerization of poly(tBMA-*b*-4VP) at 0 °C initiated by (diphenylmethyl)lithium. (a) In 99/1 vol/vol THF/HMPA: M_n(tBMA) = 4900 (M_w/M_n = 1.08); M_n(tBMA-*b*-4VP) = 11 000 (M_w/M_n = 2); composition (wt %), 73−27. (b) In 90/10 vol/vol THF/HMPA: M_n(tBMA) = 3400 (M_w/M_n = 1.1); M_n(tBMA-*b*-4VP) = 10 800 (M_w/M_n = 3.5); composition (wt %), 63−37.

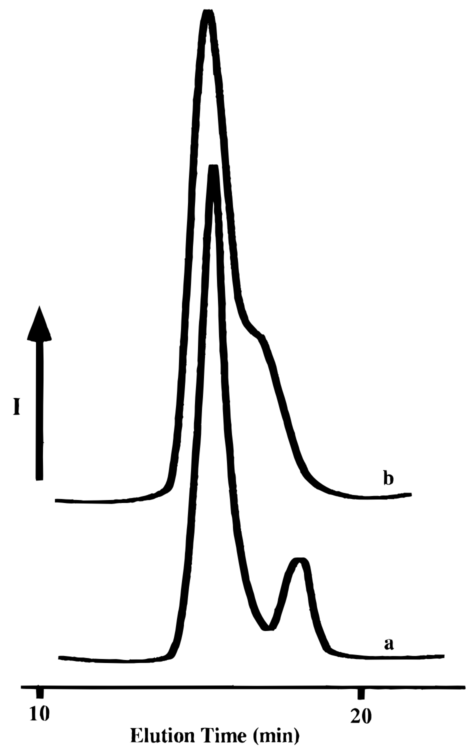


Figure 5. Anionic polymerization of poly(tBMA-*b*-4VP) at 0 °C initiated by (diphenylmethyl)lithium. (a) In 99/1 vol/vol THF/DMSO: M_n(tBMA) = 6000 (M_w/M_n = 1.09); M_n(tBMA-*b*-4VP) = 20 200 (M_w/M_n = 1.9); composition (wt %), 60−40. (b) In 99/1 vol/vol THF/NMP: M_n(tBMA) = 14 100 (M_w/M_n = 1.2); M_n(tBMA-*b*-4VP) = 27 900 (M_w/M_n = 1.6); composition (wt %), 71−29.

polymerization rate might be depressed by lithium *tert*-butoxide, which is a favorable effect. Therefore, the ratio of the crosspolymerization rate constant over the 4VP propagation rate constant might be globally increased by lithium *tert*-butoxide. In contrast, Janata et al. have shown that lithium chloride has no stabilizing effect on the tBA anions and that it reduces the propagation rate only by a factor of 3. This seems in agreement with our observation, once again within the limits of the analogy.

On the basis of the above explanation, the contamination of the copolymer by homo-PtBMA should be reduced by either increasing the reactivity of the tBMA anions or reducing the 4VP propagation rate constant. The former target might also be reached by changing the counterion, and indeed, the use of potassium instead of lithium in pure THF at 0 °C (Figure 2a) reduces the contamination of the diblock copolymer to ca. 15−20%. Unfortunately, the polymerization goes completely out of control (molecular weight distribution of 10.7) when the temperature is increased to 25 °C (Figure 2b). When carried out in a 9/1 pyridine/THF mixture, ca. 60% contamination is still observed at 0 °C, and the reaction also goes completely out of control at 25 °C. In this solvent mixture, combination of the high dielectric constant of pyridine and the high reactivity of the potassium containing ion pair has a severely detrimental effect on the copolymerization control.

Selective Additives. At this point, the complete crosspolymerization without contamination has not been reached yet. However, since the best results are observed with pyridine as cosolvent, increasing the dielectric constant of the solvent seemed at first sight to afford the best approach and was therefore further evaluated. Addition of 1% pyridine already reduces the contamination (Figure 3a), which is further lowered by adding 90% pyridine (Figure 1b) and stays so even in pure pyridine (Figure 3b). Pyridine is thus not able to totally avoid

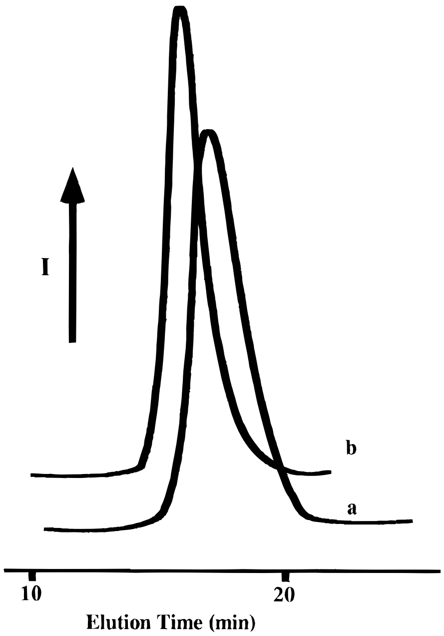
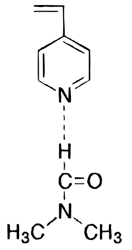


Figure 6. Anionic polymerization of poly(tBMA-*b*-4VP) at 0 °C in 99/1 vol/vol THF/DMF initiated by (diphenylmethyl)lithium. (a) M_n(tBMA) = 12 300 (M_w/M_n = 1.4). (b) M_n(tBMA-*b*-4VP) = 22 000 (M_w/M_n = 1.3). Composition (wt %): 63−37.

Chart 1



contamination. Therefore, the crosspolymerization of 4VP from PtBMA anions has been further studied in the presence of cosolvents of a higher dielectric constant ($\epsilon > 12.5$), i.e., in THF added with 1 vol % HMPA ($\epsilon = 31.3$) at 0 °C. As expected, a lower contamination is observed (Figure 4a). Contamination is, however, not further reduced upon increasing the amount of HMPA, as was observed with pyridine. Rather, the copolymerization control is partly lost in the presence of 10% HMPA (Figure 4b). When THF is now added with 1 vol % DMSO ($\epsilon = 47.2$), a low amount of contamination is once again observed at 0 °C (Figure 5a).

The crosspolymerization reaction is clearly dependent on the addition of a substance of a high dielectric constant, although contamination is not completely prevented from occurring. This is more likely due to a not selective enough activation of the tBMA anions compared to the 4VP anions.

However, the reactivity of the 4VP anions could also possibly be tuned by some additives that would interact with 4VP monomer or polyanions preferentially to the tBMA analogues. This opportunity has been evaluated by adding 1 vol % of NMP ($\epsilon = 32.5$) or DMF ($\epsilon = 38.2$) to THF. Both additives have a comparably high dielectric constant and they should accordingly affect the anions reactivity to the same extent. Nevertheless, some contamination persists in the case of NMP (Figure 5b), in contrast to DMF, which completely suppresses it (Figure 6). This striking effect might possibly be ascribed to the activation of 4VP by hydrogen bonding between the nitrogen atom and DMF (Chart 1), which makes the crosspolymerization reaction faster.

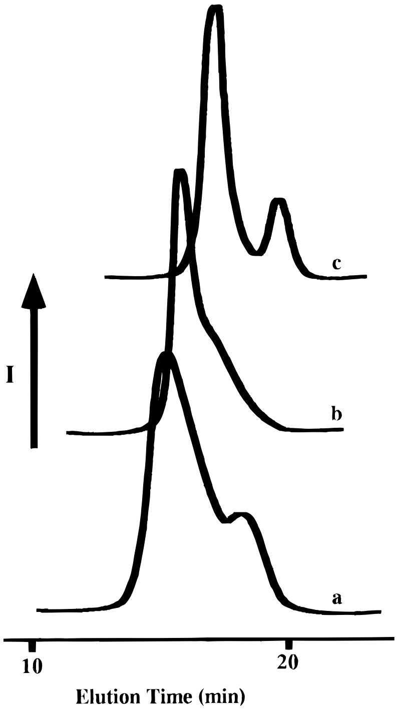
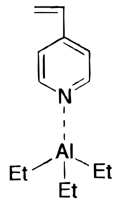


Figure 7. Anionic polymerization of poly(tBMA-*b*-4VP) initiated by (diphenylmethyl)lithium. (a) At 0 °C in 9/1 vol/vol THF/DMF: M_n(tBMA) = 4300 (M_w/M_n = 1.15); M_n(tBMA-*b*-4VP) = 14 200 (M_w/M_n = 2.8); composition (wt %), 61−39. (b) At 25 °C in 9/1 vol/vol THF/DMF: M_n(tBMA) = 7900 (M_w/M_n = 1.3); M_n(tBMA-*b*-4VP) = 18 800 (M_w/M_n = 1.8); composition (wt %), 65−35. (c) At 0 °C in 99/1 vol/vol THF/DMF (DMF is added together with 4VP): M_n(tBMA) = 3600 (M_w/M_n = 1.1); M_n (tBMA-*b*-4VP) = 10 300 (M_w/M_n = 2.2); composition (wt %), 66−34.

Chart 2



Selective activation of the 4VP comonomer seems to be a valuable way to improve the crosspolymerization between tBMA and 4VP. Nevertheless, the molecular weight distribution of the final copolymer is not very narrow. Thus, in order to improve the copolymerization reaction, lithium chloride (10-fold molar concentration of the initiator), which is known to narrow the molecular weight distribution of polymethacrylates,[7,10] has been used in addition to the 1 vol % DMF. This second additive has clearly an adverse effect on contamination. The use of a potassium counterion instead of lithium is also a way of narrowing the molecular weight distribution of PtBMA.[10] In the present case, however, replacing Li by K or sodium is no more beneficial. The same conclusion holds when the amount of DMF is increased from 1 to 10 vol % (Figure 7a), and disappointingly, an increase in temperature from 0 to 25 °C is in favor of contamination even in the presence of 1 vol % DMF (Figure 7b). Furthermore, the addition mode of DMF is also important, since the addition of DMF together with 4VP (i.e., at the second polymerization step) instead of being present from the start in the reaction

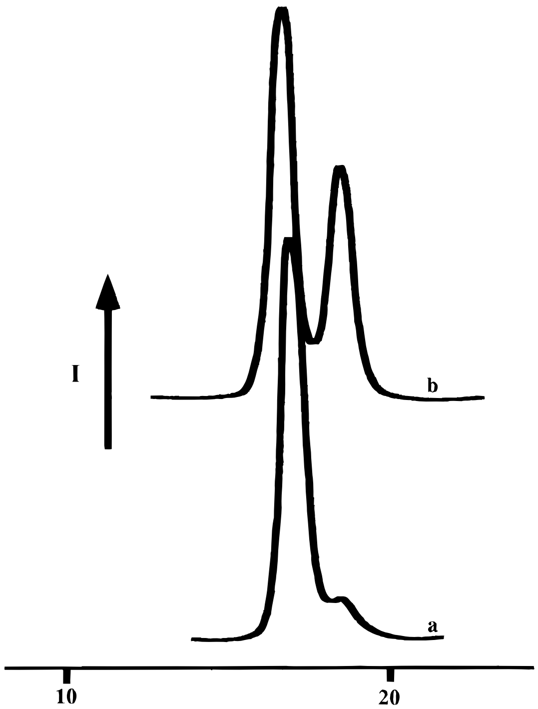
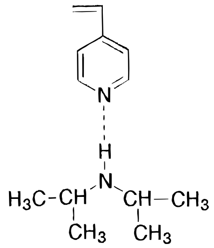


Figure 8. Anionic polymerization of poly(tBMA-*b*-4VP) in THF at 0 °C initiated by (diphenylmethyl)lithium. (a) 4VP is mixed with AlEt$_3$ before addition to the polymerization medium: M_n(tBMA) = 4000 (M_w/M_n = 1.1); M_n(tBMA-*b*-4VP) = 10 200 (M_w/M_n = 1.2); composition (wt %), 70–30. (b) AlEt$_3$ is added to the polymerization medium directly before 4VP: M_n(tBMA) = 5500 (M_w/M_n = 1.07); M_n(tBMA-*b*-4VP) = 10 000 (M_w/M_n = 1.6); composition (wt %), 63–37.

Chart 3



medium, is unfavorable to the copolymerization control (Figure 7c). Thus, although efficient under very specific conditions, the use of DMF is a tricky tool since it strongly depends on the experimental conditions.

"Winning" Ligand Combination. A more complexing additive of 4VP is expected to be of a more general beneficial use. One of the strongest complexing agents for 4VP is triethylaluminum (Chart 2). However, AlEt$_3$ was used in a low molar ratio compared to 4VP, since a higher concentration rapidly initiates 4VP polymerization before addition to the polymerization medium. In order to selectively activate 4VP, this additive was added to 4VP prior to their common injection into the reaction medium containing the living PtBMA chains.

Addition of AlEt$_3$ ($^1/_{50}$th-fold the molar concentration of 4VP) to 4VP indeed gives rise to the nearly complete disappearance of contamination (Figure 8a). In contrast, if triethylaluminum (at the same concentration) is added to the reaction medium just prior to 4VP, contamination is very high (Figure 8b). The appropriate activation of 4VP is thus a very promising method.

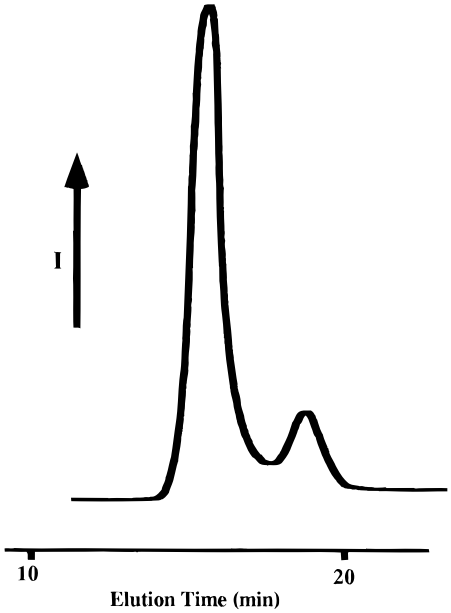


Figure 9. Anionic polymerization of poly(tBMA-*b*-4VP) in THF at 0 °C initiated by (diphenylmethyl)lithium. 4VP is added with DiPA in 2/3 vol/vol 4VP/DiPA prior to addition to the polymerization medium: M_n(tBMA) = 3500 (M_w/M_n = 1.1); M_n(tBMA-*b*-4VP) = 14 000 (M_w/M_n = 2.5); composition (wt %), 57–43.

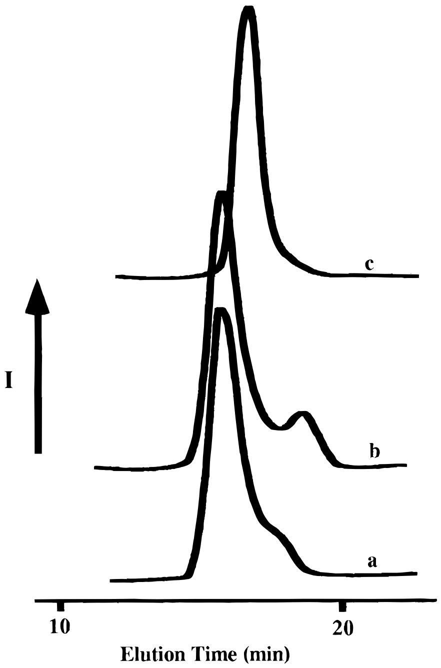


Figure 10. Anionic polymerization of poly(tBMA-*b*-4VP) in THF at 0 °C initiated by (diphenylmethyl)lithium. (a) 4VP is added with DiPA (2/3 vol/vol 4VP/DiPA) and AlEt$_3$ prior to addition to the polymerization medium: M_n(tBMA) = 5400 (M_w/M_n = 1.1); Mn(tBMA-*b*-4VP) = 17 500 (M_w/M_n = 1.5); composition (wt %), 54–46. (b) 4VP is added with DiPA and DMF (2/3/2 vol/vol/vol 4VP/DiPA/DMF) prior to addition to the polymerization medium: M_n(tBMA) = 4200 (M_w/M_n = 1.14); M_n(tBMA-*b*-4VP) = 12 900 (M_w/M_n = 1.9); composition (wt %), 64–36. (c) 4VP is added with DMF (1/1 vol/vol 4VP/DMF) and AlEt$_3$ prior to addition to the polymerization medium: M_n(tBMA) = 3400 (M_w/M_n = 1.14); M_n(tBMA-*b*-4VP) = 10 200 (M_w/M_n = 1.27); composition (wt %), 66–34.

Another way to activate 4VP is through hydrogen bonding with an amine, such as diisopropylamine (Chart 3).

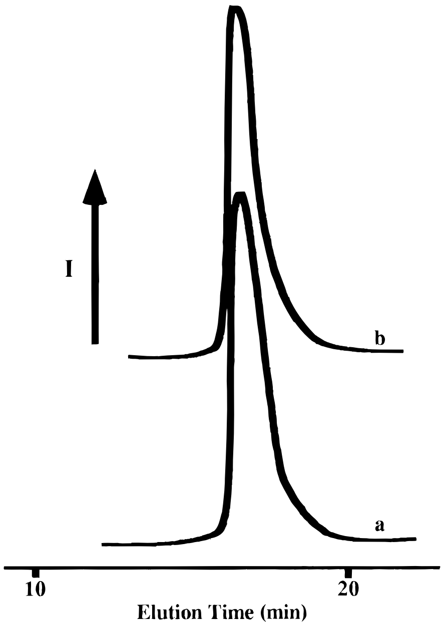


Figure 11. Anionic synthesis of poly(tBMA-*b*-4VP) in THF initiated by (diphenylmethyl)lithium. 4VP is added with DiPA/DMF/$AlEt_3$ (2/3/2 vol/vol/vol 4VP/DiPA/DMF)): (a) (at 0 °C) M_n(tBMA) = 4500 (M_w/M_n = 1.09), M_n(tBMA-*b*-4VP) = 13 500 (M_w/M_n = 1.19), composition (wt %) 66−34; (b) (at 25 °C) M_n(tBMA) = 4200 (M_w/M_n = 1.14), M_n(tBMA-*b*-4VP) = 11 600 (M_w/M_n = 1.22), composition (wt %) 71−29.

Indeed, the contamination is strongly reduced when 4VP is mixed with DiPA in 1/1.5 4VP/DiPA vol/vol ratio (Figure 9), despite the low dielectric constant of DiPA ($\epsilon = 2.9$ reported value for dipropylamine, which should be comparable to that of DiPA). The decrease in contamination seems to parallel the capability of the additive to interact with 4VP: the stronger the interaction, the lower the contamination. According to our observations, the most efficient additives are DMF, DiPA, and triethylaluminum. Moreover, if they are paired, some further improvement is still possible (Figure 10a−c), but the best result is obtained (Figure 11a) when the three additives are used together, even at 25 °C (Figure 11b). Although already very efficient in itself, $AlEt_3$ should thus be preferably combined with DMF or DiPA, since less complications due to autoinitiation of 4VP upon $AlEt_3$ addition are observed in the presence of one of these two additives.

Conclusion

The "classical" anionic block copolymerization of tBMA with 4VP has been shown to afford contamination of the final product by homo-PtBMA. This contamination, the amount of which strongly depends on the solvent, has proved to be due not to side reactions, as initially suspected, but to a reactivity mismatch of the two monomers. Their relative reactivity can be somewhat tuned either by a solvent of a high dielectric constant or by switching from Li to K cation. Nevertheless, complete removal of contamination requires the simultaneous specific activation of 4VP via the interaction of the nitrogen lone pair with an adequate additive (AlR_3, amines, DMF). This highlights the interesting possibility of modulating the apparent relative reactivity of monomers through specific interactions.

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