Anionic Homopolymerization and Block Copolymerization of 4-Vinylpyridine and Its Investigation by High-Temperature Size-Exclusion Chromatography in *N*-Methyl-2-pyrrolidinone

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ABSTRACT: The low-temperature homopolymerization and block copolymerization of 4-vinylpyridine (4VP) initiated with monofunctional alkali-metal-based carbanionic species have been studied in tetrahydrofuran (THF), THF/hexamethylphosphoric triamide (THF/HMPT), or THF/dimethylformamide (THF/DMF) solvent mixtures. The polymers were analyzed by size-exclusion chromatography (SEC) in *N*-methyl-2-pyrrolidinone (NMP) at 90 °C. Elution in NMP at 90 °C is possible without adsorption of the poly(4-vinylpyridine) using a μ-Styragel packing material. The reported experimental conditions allow the high-yield synthesis of P4VP samples without contamination with branched material. The P4VP samples have a predetermined molecular weight and a very low polydispersity. Well-defined AB type diblock and ABA type triblock copolymers of 4VP with methacrylate monomers were prepared by sequential monomer addition initiated by different monofunctional initiators. Crossover propagation reactions from P4VP macroanions to methacrylate monomers and vice versa were demonstrated by size-exclusion chromatography.

Introduction

The discovery by Szwarc[1] that some monomers can be polymerized by a "living" process has provided a very powerful tool for the control of architecture, molecular weight, and polydispersity of homopolymers. The living polymerization process makes possible the synthesis of block polymers, star polymers, macromonomers, and functionalized polymers, e.g., telechelics.[2]

The anionic polymerization of hydrocarbon monomers such as styrene or dienes to yield well-controlled block copolymers has been known for more than 2 decades.[3] However, very recently it has also been demonstrated that alkali-metal-based initiators modified with lithium halides are able to initiate and to control precisely the homopolymerization and block copolymerization of polar monomers such as (meth)acrylic esters.[4–7] In the absence of these initiator systems, polymerization of these monomers is normally accompanied by various secondary reactions. The approach is now being explored commercially.[8]

In recent years, considerable interest has been shown in the anionic polymerization of 4-vinylpyridine homopolymers and various block copolymers with oxiranes and some methacrylic esters. The potential applications of these materials are primarily in the area of biomedical engineering as well as the production of thermoplastic elastomers. The possibility of using either 2-vinylpyridine or 4-vinylpyridine offers further options in that ionomeric segments can be produced by quaternization of the pyridyl nitrogen with a variety of alkyl halides or inorganic acids.[9–12] For steric reasons, the quantitative quaternization of the nitrogen on aromatic rings is more easily performed for 4-vinylpyridine than for 2-vinylpyridine. While anionic polymerization of 2-vinylpyridine is relatively straightforward and is accompanied by only limited secondary reactions,[13–17] considerable complications arise with 4-vinylpyridine.[18–20] These complications include the presence of enhanced secondary reactions involving a –N=CH– unit of the aromatic ring in the para position with the growing active center, which can result in either covalent or ionic structures. These newly generated active centers are also capable of initiating polymerization, which means that the polymers produced in this way can be a mixture of linear as well as branched material.[19] Another complication that arises in this connection is that solvents which are commonly suitable for the anionic polymerization, for instance, THF or diglyme, are nonsolvents for P4VP above a certain molecular weight, which results in a heterogeneous polymerization. As a consequence of these complications, only a few studies have been devoted to the homopolymerization and copolymerization of 4VP. Still another reason for the paucity of studies is the fact that homo-4VP or its copolymers cannot be eluted or are only partially eluted through SEC columns using solvents such as THF, $CHCl_3$, or DMF, the most commonly used eluents.[21] Thus, this most powerful tool for the study of the polymerization products cannot be applied effectively in this particular case.

The purpose of this paper is to describe anionic polymerization techniques for the production of linear homo-4VP of low polydispersity as well as its block copolymers with methacrylates. The paper also describes an SEC process which permits the study of these materials. We believe that both of these aspects are novel. The polymerization of 4VP by anionic techniques to yield the material of low polydispersity is of interest in itself. While there are some claims in the literature for the production of this kind of material, the elution by SEC of these polymers is unable to confirm the molecular dispersity of the materials, because of difficulties in the use of the SEC technique. The first part of the paper is devoted to a description of the homopolymerization of 4VP and its study by SEC. The second part will explore the block copolymerization of these 4VP polymers of low polydispersity with methacrylate monomers, such as methyl methacrylate and *tert*-butyl methacrylate. These methacrylate monomers were selected since the kinetics of their homopolymerization are well understood.

Experimental Section

Methyl methacrylate (MMA) and *tert*-butyl methacrylate (tBuMA) obtained from Aldrich were first vacuum distilled from CaH_2 after reflux and then stored under a nitrogen atmosphere

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Table I
Data for the Polymerization of 4VP Initiated by α-MS$^-$Li$^+$ at −78 °C[a]

code	solvent	initiator quantity (mmol)	4VP quantity (mol)	yield (%)	M_n(calc)[b]	M_n(SEC)	M_w/M_n	f[c]	reaction medium
132	THF	0.90	0.041	100	4 900	5 000	1.10	0.97	yellow clear soln
138	THF	0.90	0.076	95	8 400	9 000	1.35	0.93	yellow opaque soln
138′	THF	0.13	0.052	85	31 700	37 500	1.40	0.84	yellow opaque soln
136	THF/HMPT	0.44	0.052	100	12 500	14 000	1.15	0.89	yellow clear soln
135	THF/HMPT	0.20	0.052	100	27 500	28 500	1.15	0.96	yellow opaque soln
134	THF/HMPT	0.12	0.052	100	46 000	49 000	1.20	0.93	yellow opaque soln
113	THF/HMPT[d]	0.48	0.052	100	10 500	10 200	1.05	1.02	yellow opaque soln

[a] The polymerization time was 15 min, and the polymer concentration was 1%. [b] M_n(calc) = $105[M]_0/[I]_0 \times$ % conversion. [c] Initiator efficiency = concentration of active centers/$[I]_0$. [d] LiCl was added: the LiCl:[I] molar ratio was 5.

at −20 °C. Prior to the polymerization, the 4VP was stirred over a sodium mirror until a light yellow developed. It was then redistilled under reduced pressure just before the polymerization. A 10 wt % triethylaluminum solution in hexane was added to the MMA or the tBuMA until a persistent yellowish-green was observed.[22] The monomer was then redistilled under reduced pressure just prior to polymerization.

THF was purified by refluxing over a fresh sodium–benzophenone complex (a deep purple indicating an oxygen- and moisture-free solvent). DMF was dried by refluxing over P_2O_5 for 48 h and was then distilled and subsequently kept under a positive nitrogen pressure. It was treated with BaO overnight (to remove any formic acid impurities) and redistilled over 3-Å molecular sieves. Distilled DMF was treated with diphenylmethylpotassium (a persistent red-orange was observed) and stored at −20 °C. Finally, the DMF was redistilled just before the polymerization. Hexamethylphosphoric triamide (HMPT) was purified by refluxing over P_2O_5, distilled, and treated dropwise with oligomeric poly(styryllithium) until a persistent orange-red was seen. This was followed by redistillation under reduced pressure.

The initiators used in this study were α-methylstyryllithium (α-MS$^-$Li$^+$), 1,1-diphenyl-3-methylpentyllithium (DPP$^-$Li$^+$), or diphenylmethylpotassium ($Ph_2CH^-K^+$). α-MS$^-$Li$^+$ and DPP$^-$Li$^+$ are the reaction products of *sec*-butyllithium with a few units of α-methylstyrene and one unit of diphenylethylene, respectively. $Ph_2CH^-K^+$ was prepared at room temperature by reacting diphenylmethane with potassium naphthalene in THF for 24 h.[23]

Polymerization. Anionic homopolymerization and block copolymerization of 4VP with methacrylates was carried out in a flamed-glass reactor under a nitrogen atmosphere. Solvent(s) and initiator were transferred into the glass reactor using a rubber septum and a stainless steel capillary or a syringe. The initiator solution was added dropwise to the solvent until the initiator color persisted. The addition of 4 or 5 drops of a 0.2 M initiator solution to 500 mL of solvent was generally required to get a persistent color, indicating a pure solvent.

Homopolymerization of 4VP. After adding the desired amount of the initiator to the THF, the solution was cooled to −78 °C. The monomer was diluted with THF (1/1, v/v). The required quantity of 4VP was added slowly. A sudden change of the color of the initiator from red to light yellow (in the case of α-MS$^-$Li$^+$ and DPP$^-$Li$^+$) was noticed. The polymer concentration was kept at about 1%. The polymerization was terminated with methanol, and a clear or milky solution was obtained depending on the chain length of P4VP. The polymer was recovered by precipitation in hexane. For the homopolymerization of 4VP in a THF/DMF mixture (4/1, v/v), $Ph_2CH^-K^+$ was used as the initiator. After adding few drops of the monomer at −78 °C, the red-orange of the initiator darkened further. For the whole range of molecular weights listed in Table II, the polymerization solutions were homogeneous. The polymerization was terminated with methanol, and a colorless solution was obtained. The polymer was recovered by removing the solvent under reduced pressure and redissolving the polymer in a THF/methanol (9/1, v/v) mixture, followed by precipitation in cold hexane. The polymer was dried at 80 °C for 48 h under vacuum.

Block Copolymerization of 4VP with Methacrylic Esters. The anionic block copolymerization of 4VP with tBuMA or with MMA was carried out in a flamed-glass reactor under a nitrogen atmosphere using a technique similar to that for the homopolymerization of 4VP. The same monofunctional alkali-metal-based initiators as were used for the homopolymerization of 4VP were employed to initiate the block copolymerization. Block copolymers were achieved by sequential monomer addition of monomers. An aliquot of the reaction medium was withdrawn at each step for an analysis by SEC in order to determine the molecular weight of each block. The polymerization was stopped by adding methanol, and the block copolymers were recovered by precipitation in hexane. For the block copolymerization that was carried out in the THF/DMF solvent mixture, the polymer was recovered after removing the solvents under reduced pressure and redissolving the polymer in a THF/methanol (9/1, v/v) solvent mixture, followed by precipitation in cold hexane. The crude polymer was dried under vacuum at 80 °C for 48 h.

Size-Exclusion Chromatography (SEC). The SEC measurements were performed on a Waters CV150 high-temperature liquid chromatography apparatus equipped with a refractive index detector. The column was a high-temperature μ-Styragel linear mixed-bed HT column, obtained from Waters. The concentration of the injected polymer solution was about 2 mg/mL. The solution was filtered through membrane filters before injection. At first common solvents such as THF, $CHCl_3$, and DMF were tried as carrier solvents for the homopolymers and block copolymers of 4VP with methacrylates using μ-styragel columns. It was observed that block copolymers even with the lowest 4VP (5 wt %) contents could not be eluted either in THF or in $CHCl_3$ at a column temperature of 40 °C. By contrast, however, if NMP was used as an eluent at 90 °C, the homopolymer as well as block copolymers of 4VP with methacrylates and styrene were eluted without any noticeable adsorption. This was ascertained from the fact that the ratio of the total peak area (A in arbitrary units for the system) to the polymer concentration (C in grams per liter) for the P4VP was approximately equal to that found for polystyrene (A/C = (1.92 ± 0.15) × 10^6 for polystyrene and A/C = (1.88 ± 0.14) × 10^6 for P4VP). The molecular weights and the polydispersity indices were calculated according to the calibration with polystyrene standards.

Results and Discussion

Homopolymerization in THF. Table I reports the data for the polymerization of 4VP in THF using α-MS$^-$Li$^+$ as an initiator. 4VP was added to the polymerization medium as a dilute solution (50% in THF v/v) rather than as the pure monomer; otherwise, the monomer could polymerize locally, giving rise to various secondary reactions before being dispersed in the reaction medium. The red of the initiator changed instantaneously to a light yellow upon the addition of a few drops of monomer. The homopolymerization was a very rapid and exothermic reaction. The initiation of 4VP can be faster than the propagation, since the products (see below) have a fairly narrow molecular weight distribution. The monomer conversion was quantitative in all cases. For molecular weights <5000 (DP of ca. 45), the polymerization medium was found to be clear and of a light yellow color. However, as the P4VP macroanions grew beyond ca. 45 units, the

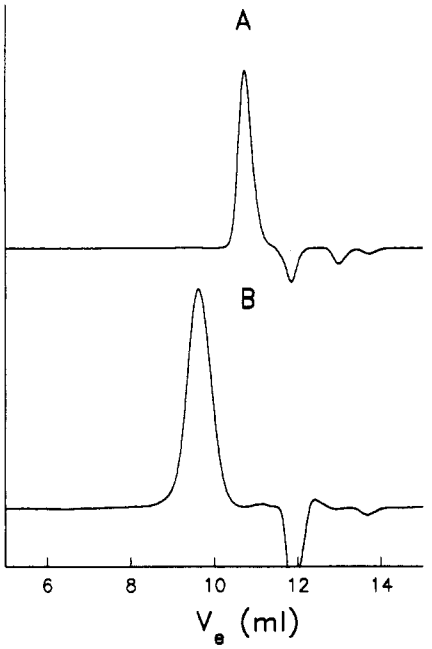

Figure 1. Size-exclusion chromatograms of P4VP prepared in THF using α-MeSt$^-$Li$^+$ as the initiator at −78 °C: (A) M_n = 5000, M_w/M_n = 1.10 (Table I, entry no. 1); (B) M_n = 9000, M_w/M_n = 1.35 (Table I, entry no. 2).

polymerization solution became opaque. After termination of the reaction with a few drops of methanol, the light yellow changed to a blue opalescent tint (Table I, entry no. 1) and to a milky solution for higher molecular weights (Table I, entry nos. 2 and 3). The dried crude P4VP with a DP of ca. 45 was found to be soluble in THF, CH_3OH, $CHCl_3$, etc. In contrast to the above findings, Tardi and Sigwalt[18] have reported that P4VP of DP ca. 20 was insoluble in THF. Their UV measurements for the living macroanions of 4VP suggested the involvements of secondary reactions in the very early stages of polymerization of 4VP in THF. P4VP of M_n 9000 (Table I, entry no. 2) was found to be insoluble in THF, although a clear solution was obtained in a THF/CH_3OH (9/1, v/v) solvent mixture.

Figure 1 shows the chromatograms of P4VP (Table I, entry nos. 1 and 2) of the crude polymer synthesized in THF at −78 °C. The SEC analysis shows that the homopolymer of M_n 5000 has a M_w/M_n of 1.10. A slight broadening of the molecular weight distribution was noticed when the M_n was higher than 5000 (M_w/M_n > 1.30). In the table the experimental M_n values are compared to those calculated from the monomer/initiator molar ratio and conversion assuming a living process (M_n(calc) = 105 $[M]_0/[I]_0$ × % conversion) where $[M]_0$ and $[I]_0$ are the initial monomer and initiator concentrations; the values are close. Experimental data indicate that a fraction of the initiator was lost, most likely during the initiation step, because of reactions with impurities in the monomer. The initiator efficiency f (given by the concentration of growing chains divided by the concentration of the initiator, i.e., $[P]/[I]_0$) is clearly over 90%.

Polymerization of 4VP in a THF/HMPT (9.9/0.1, v/v) Mixture. THF/HMPT mixtures are also good solvents for homo-4VP. The homopolymerization was carried out at −78 °C in the presence of 1% HMPT in THF using α-MS$^-$Li$^+$ as the initiator. The polymer concentration was kept at about 1%. The initiation of 4VP was instantaneous, as indicated by the change of the deep red of the initiator to yellow. The data for this system are also seen in Table I. It is worth noting that, in the presence of 1% HMPT, the polymer solution of P4VP macroanions with an M_n of 14 000 (Table I, entry no. 4) was found to be clear; however, increasing the length of P4VP macroanions beyond that point turns the solution opaque. The SEC analysis again showed the polymer to be unimodal with an M_w/M_n = 1.20. There was no sign of high molecular weight species which could be detected by SEC resolution. The polymerization in the presence of a 5-fold excess of LiCl in the initiator resulted in a highly monodisperse polymer in contrast to the slightly broader distribution without LiCl. The kinetics of the polymerization reaction of 4VP in the presence of LiCl are under investigation and will be published later.

Table II
Data for the Polymerization of 4VP Initiated by $Ph_2CH^-K^+$ in a THF/DMF (8/2 v/v) Solvent Mixture at −78 °C[a]

code	initiator (mmol)	M_n(calc)	M_n(SEC)	M_w/M_n	
108	0.80	6 200	7 100	1.05	0.87
110	0.26	19 300	20 600	1.15	0.93
	0.08	62 500	67 000	1.18	0.93
141[b]	0.40	12 500	15 400	1.60	0.81
			892 000	1.20	

[a] The polymerization time was 15 min, and the polymer concentration was 2.5%. 4VP = 0.0476 mol. Polymer yield was 100%. [b] Polymerization temperature was 0 °C.

Polymerization of 4VP in THF/DMF (4/1, v/v) Mixtures. DMF is known to be a good solvent for the homo-4VP; however, its use is limited in anionic polymerization, mainly because of the many steps involved in its purification. Furthermore, the recovery of P4VP is difficult since DMF is immiscible with the generally used nonsolvents for P4VP such as ether or heptane. In spite of these drawbacks, it was of interest to look for a DMF-based solvent system that could be used for the homogeneous anionic "living" polymerization of 4VP to yield homopolymer and block copolymer with many copolymerizable monomers and a broad range of molecular weights.

The homopolymerization of 4VP was carried out in a 4/1 (v/v) THF/DMF solvent mixture, and the total polymer concentration was kept at 2%. The initiator chosen was diphenylmethylpotassium ($Ph_2CH^-K^+$), since the α-MS$^-$Li$^+$ initiator was found to be unstable; i.e., no persistent red was observed. The $Ph_2CH^-K^+$ initiator in the THF/DMF solvent medium developed a deep red-orange. After the addition of a few drops of monomer, the color of the initiator darkened slightly. Table II shows that using $Ph_2CH^-K^+$ as the initiator for the polymerization of 4VP at −78 °C again allows precise architectural control to yield highly monodisperse linear homo-4VP with an M_w/M_n of 1.15. It is interesting to note that, in the synthesis of P4VP macroanions of an M_n of 67 000, the polymerization medium retained a clear deep-red-orange without any noticeable opaqueness. The termination of the reaction with methanol resulted in a colorless clear solution. The monomer conversion was found to be quantitative, in all cases with a high initiator efficiency (over 90%).

In order to demonstrate that the macroanions are long-lived, monomer resumption experiments were performed in the same solvent mixture. A total of 0.048 mol of 4VP was first polymerized using 1.3×10^{-3} mol of $Ph_2CH^-K^+$ as the initiator. The M_n(expt) was 4200, and the M_w/M_n was 1.09. Then 0.142 mol of another monomer was added after 15 min. The final polymer had an M_n of 15 500 and an M_w/M_n of 1.15. The SEC traces indicated the absence of any noticeable deactivation of the polymacroanions of 4VP of the first batch. The SEC traces are given in Figure 2.

The effect of temperature on the polymerization of 4VP in the THF/DMF solvent mixture has also been investi-

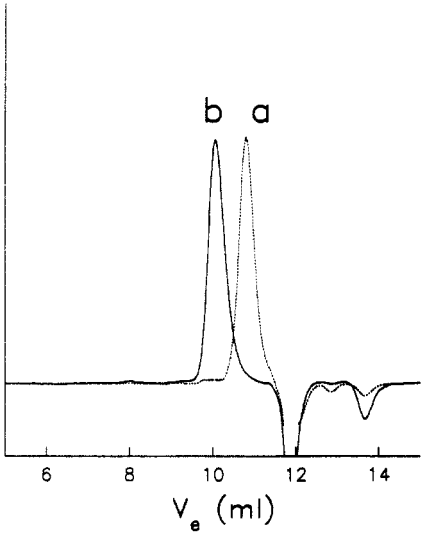

Figure 2. Size-exclusion chromatograms of P4VP prepared in a THF/DMF (4/1, v/v) solvent mixture using $Ph_2CH^-K^+$ as the initiator: (a) after polymerization of the first monomer; (b) after polymerization of the second monomer.

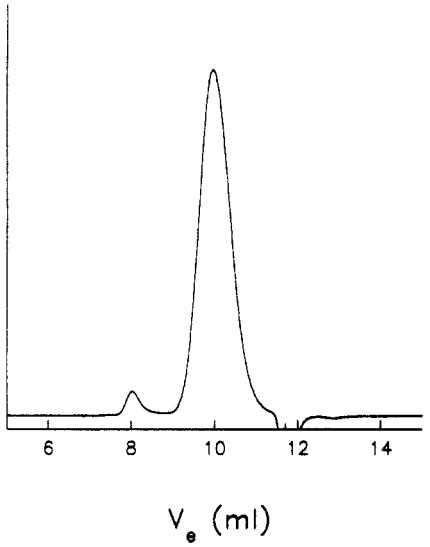

Figure 3. Size-exclusion chromatogram of P4VP prepared in a THF/DMF (4/1, v/v) solvent mixture using $Ph_2CH^-K^+$ as the initiator at 0 °C (Table II, entry no. 4).

gated. One reaction was carried out at 0 °C. The monomer conversion was quantitative. SEC analysis of the crude product showed a bimodal distribution (see Figure 3). The major fraction of the polymer, ca. 93% (on the basis of the area of the SEC trace), had an M_n of 15 400 with an M_w/M_n of 1.60. A higher molecular weight species is also observed, ca. 7% which shows an M_n of 890 000. This suggests that the polymerization of 4VP at 0 °C may be accompanied by one or more secondary reactions. It has been suggested that these high molecular weight species consist of branched material.[18,20] In this particular case, the degree of branching for the high molecular weight fraction indicates a value of 58 branches per cross-linked core calculated on the basis of SEC retention times. Tardi and Sigwalt[18] suggested several possible secondary side reactions in the anionic homopolymerization of 4VP carried out at low temperature in THF, some of which are accelerated by an intramolecular mechanism resulting from a resonance-stablized structure involving electron delocalization of 4-pyridyl carbanions onto nitrogen (-N=CH-). Luxton et al.[19] suggested that these reactions can be further enhanced by the solvation of the counterion by the P4VP chains acting as a polydentate complexing agent. The degree of branching depends on the competition between the normal vinyl polymerization and the secondary reaction of the growing active center with -N=CH-. The secondary reaction makes 4-vinylpyridine a bifunctional monomer just as divinylbenzene. This reaction may have a higher activation energy than the vinyl polymerization. Therefore, the branching can be decreased and even avoided by lowering the reaction temperature.

The results of the polymerization runs at -78 °C demonstrate that it is possible to obtain P4VP of predetermined molecular weight and very low polydispersity. The agreement between the calculated and experimental molecular weights implies further that the homo-4VP polymers have no branched component as verfied by their size-exclusion chromatograms.

Poly(4VP-*b*-*t*BuMA) Diblock Copolymers. The foregoing section has demonstrated that the polymerization of 4VP in a suitable solvent mixture can produce a linear monodisperse material. This allows at least potentially the controlled block copolymerization of 4VP with a number of nonpolar (cyclic as well as vinyl monomers) and polar monomers, e.g., (meth)acrylic esters. In block copolymerization reactions, it is essential to know whether the macroanions derived from one polymer are able to initiate quantitatively the living polymerization of the second comonomer. The cross-reactivity of the comonomer pair in an anionic process is crucial for the successful synthesis of tri- or multiblock copolymers by successive addition of monomers involving multiple steps. The first approach in this direction was to investigate the anionic block copolymerization of a methacrylate ester initiated by macroanions of 4VP. The initiators α-MS^-Li^+ and $Ph_2CH^-K^+$ were used, and the polymerization was carried out in THF/HMPT or in THF/DMF solvent mixtures. Table III reports the experimental values for the molecular weights, and the polydispersity (M_w/M_n) of the block copolymers. The conversion of the comonomers was quantitative in all cases, and the reaction medium was homogeneous.

The block copolymerization of 4VP with *tert*-butyl methacrylate initiated by α-MS^-Li^+ initiator in THF/HMPT (Table III, entry no. 1) resulted in materials of low polydispersity for both the prepolymers of P4VP (M_n 14 000 and M_w/M_n = 1.15) and its subsequent diblock copolymer with tBuMA (M_n = 22 000 and M_w/M_n = 1.20). The experimental molecular weights, as determined by SEC with polystyrene standards, were close to the theoretical values.

The initiation of the tBuMA by the living macroanion of 4VP in a THF/DMF solvent mixture was also investigated. Living 4VP macroanions with an M_n of 14 000 and a M_w/M_n of 1.10 were prepared using $Ph_2CH^-K^+$ as the initiator followed by the addition of tBuMA monomer. The block copolymer shows a broadening in its MWD (M_w/M_n = 1.45) with a quantitative comonomer conversion. The SEC analysis of the final product did not indicate any enhancement of the number-average molecular weight, while the SEC peak elution maxima shifted to a lower elution volume (Table III, entry no. 2). The broadening of the molecular weight distribution of the block copolymer in THF/DMF suggests the presence of secondary reactions.

Poly(*t*BuMA-*b*-4VP) Diblock Copolymers. To demonstrate the feasibility of the reverse reaction sequence, living PtBuMA macroanions were first prepared in THF or a THF/DMF solvent mixture using $Ph_2CH^-K^+$ as the initiator. As suggested in discussing the data of Table I (entry no. 1), as the living polymacroanions of 4VP grew

Table III
Data for the AB Diblock Copolymers of 4VP with Methacrylates, Synthesized at −78 °C in THF, THF/HMPT, and THF/DMF Solvents Using Monofunctional Alkali-Metal Initiator[a]

code	solvent	initiator (mmol)	monomer (mol) A	monomer (mol) B	molecular A block M_p[b]	molecular A block M_n	molecular A block M_w/M_n	features for diblock M_p[b]	features for diblock M_n	features for diblock M_w/M_n
136	THF/HMPT	α-MSLi (0.44)	4VP (0.052)	tBuMA (0.021)	18 000	14 000	1.15	29 000	22 000	1.20
146	THF/DMF	Ph_2CHK (0.44)	4VP (0.047)	tBuMA (0.030)	17 000	14 000	1.10	20 000	14 000	1.45
149	THF	Ph_2CHK (0.60)	tBuMA (0.014)	4VP (0.047)	3 950	3 800	1.10	17 000	13 700	1.15
140	THF/DMF	Ph_2CHK (0.40)	tBuMA (0.035)	4VP (0.047)	12 000	13 500	1.10	30 500	20 000	1.50
145	THF/DMF	Ph_2CHK (0.40)	MMA (0.020)	4VP (0.040)	5 000	5 500	1.15	20 000	17 000	1.25

[a] The block copolymerization time was 30 min, and the polymer concentration was 2.5%. [b] M_p is the peak molecular weight of the chromatograms.

beyond approximately 50 units per chain in THF at −78 °C, an opaque yellow solution is formed. Furthermore, it has been suggested that the solubility of P4VP in THF can be modified to some extent when the 4VP is attached to another block which is soluble in THF.[24-26] The solubility limit of P4VP in THF now appears to depend on the molar ratio of each block.

The data for the block copolymerization of tBuMA with 4VP are also given in Table III. Poly(*tert*-butyl methacrylate) macroanions of 27 and 85 units with an M_w/M_n of 1.10 were used to initiate the 4VP. The light yellow of the $PtBuMA^-K^+$ changed instantaneously to a dark-yellow-orange after the addition of a few drops of 4VP monomer. The solution remained homogeneous for the quantity of 4VP used in the present block copolymerization. The SEC analysis showed that the block copolymer prepared in THF was fairly monodisperse, with an M_w/M_n of 1.15. However, for the block copolymer prepared in THF/DMF solvent mixtures, a broadening in the molecular dispersity was found with an M_w/M_n of 1.45. By contrast, the block copolymerization of MMA with 4VP in THF/DMF solvent mixtures yielded a block copolymer of fairly narrow dispersity. The M_n for the first PMMA block was 5500, and the M_w/M_n was 1.15, while the block copolymer showed an M_n of 17 000 with an M_w/M_n of 1.25.

Triblock Copolymers. Since there is no problem of cross-reactivity, the sequential anionic polymerization of methacrylate monomer and 4VP was attempted. The synthesis of triblock copolymers should represent a straightforward extention of the results discussed in the foregoing section. It is feasible to prepare ABA or BAB type block copolymers by using either a difunctional initiator in two steps or a monofunctional initiator involving three steps by sequential monomer addition. A P(tBuMA-*b*-4VP-*b*-tBuMA) triblock copolymer was prepared in THF using the $Ph_2CH^-K^+$ (0.3 mmol) monofunctional initiator at −78 °C. Poly(tBuMA) macroanions (7.0 mmol) of a DP of 26 units, with an M_w/M_n of 1.10, were used to initiate 4VP (0.024 mmol). The resulting diblock had an M_n of 11 000 with an M_w/M_n of 1.15. In the third step, tBuMA (55 mmol) was added. The deep yellow of the polymerization medium once again changed to a light yellow. The resulting final product had an M_n of 40 000 and an M_w/M_n of 1.25. The SEC traces are represented in Figure 4. P(4VP-*b*-tBuMA-*b*-4VP) can also be prepared using a similar strategy using various types of alkali-metal-based initiators. This multistep sequential anionic polymerization can be extended to other (meth)acrylic esters of low T_g in order to develop a new family of thermoplastic elastomers, ensuring further development of a valuable class of ionomers.

Conclusion

Suitable experimental conditions for the polymerization of 4VP have been described that can yield linear homopolymers of low polydispersity as well as different types of block copolymers. It has also been shown that polymerization reactions for these polymers can now be monitored by SEC without sample adsorption or elution retardation. The experimental techniques and the analysis of the polymers by SEC open the possibility for the molecular engineering of 4VP-based materials such as polymeric emulsifiers, electrically anisotropic heterophase materials, biomaterials, etc.

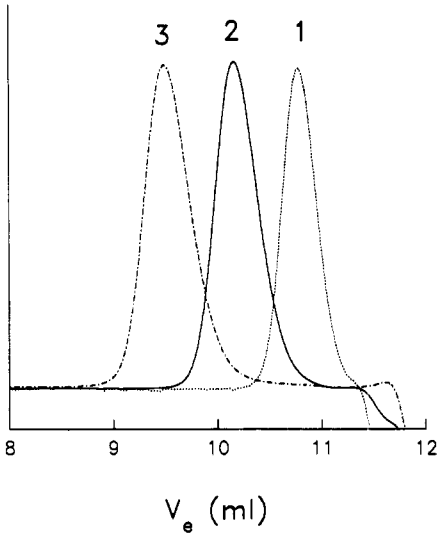

Figure 4. Size-exclusion chromatograms of (1) P(tBuMA), M_n = 3700, M_w/M_n = 1.10; (2) P(tBuMA-*b*-4VP), M_n = 11 000, M_w/M_n = 1.20; and (3) P(tBuMA-*b*-4VP-*b*-tBuMA), M_n = 40 000, M_w/M_n = 1.25.

References and Notes

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