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Synthesis and Characterization of Narrow Molecular Weight Distribution AB and ABA Poly(vinylpyridine)−Poly(dimethylsiloxane) Block Copolymers via Anionic Polymerization

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ABSTRACT: The synthesis is described of AB and ABA narrow molecular weight distribution poly(2-vinylpyridine)−poly(dimethylsiloxane) (P2VP−PDMS) and poly(4-vinylpyridine)−poly(dimethylsiloxane) block copolymers. Three synthesis methods were explored. The first and most general procedure (method 1) involves the anionic polymerization of 2VP or 4VP initiated by an acetal-functionalized alkyllithium. Acid hydrolysis of the acetal and titration of the resulting hydroxyl group with triphenyllithium gave a lithium alkoxide end group. This functionality was used to initiate hexamethylcyclotrisiloxane (D_3), giving the living P2(4)VP-*b*-PDMSLi block copolymers that were terminated or coupled with trimethylchlorosilane and dimethyldichlorosilane, respectively, to give the AB and ABA block copolymers. An alternative synthesis (method 2) applicable only to the synthesis of P2VP-*b*-PDMS or P2VP-*b*-PDMS-*b*-P2VP involved alkylation of the lithium P2VP anion with a bromo-functionalized acetal. Acetal hydrolysis and titration with triphenylmethyllithium gave the lithium alkoxide end-functionalized P2VP that was used to initiate D_3 followed by termination or coupling with trimethylchlorosilane and dimethyldichlorosilane, respectively. P2VP−PDMS block copolymers could also be synthesized (method 3) by end-capping of living P2VPLi with 2-isopropenylpyridine followed by addition of 1 equiv of ethylene oxide. Addition of D_3 to the resulting lithium alkoxide and coupling with trimethylchlorosilane or dimethyldichlorosilane gave the desired AB and ABA block copolymers.

Introduction

The synthesis of many potentially interesting block copolymers is often complicated by the failure of the active site of the first block to cleanly and rapidly initiate the monomer corresponding to the second block. There are examples of this type in anionic vinyl polymerizations where the reason for the failure to generate well-defined block copolymers is far from obvious.[1−4]

An example is the failure of the living poly(methyl methacrylate)lithium (PMMALi) to initiate hexamethylcyclotrisiloxane (D_3) in THF or toluene. In this case generation of the far less basic lithium silanolate by ring opening of D_3 by the strongly basic ester enolate[5] (pK_a of conjugate acid = 30−32) does not take place. The problem, at least in part, is the decomposition of the PMMALi under practical reaction conditions.[6] However, it is by no means clear that the initiation would readily take place in the absence of decomposition of the PMMALi. Problems involving initiation of D_3 by living polymer anions are also observed in other cases. For instance, initiation of D_3 by poly(2-vinylpyridine)lithium (P2VPLi) in THF is imperceptibly slow even at room temperature.[7,8] Although the direct initiation of D_3 by P2VPLi was reported, the initiation/polymerization required 50 °C and very long reaction times (18 h).[8] No molecular weight (MW) distributions were reported in this case, but these would be anticipated to be wide. Likewise, initiation/polymerization of D_3 by living P4VPNa in pyridine/THF took 2 days as reported by Nugay et al.[9] Even polystyryllithium (PSLi) is a relatively poor initiator in THF even at room temperature.[10] For instance, Saam et al. reported the synthesis of polystyrene-*b*-poly(dimethylsiloxane) (PS-*b*-PDMS) in cyclohexane/THF by initiating styrene with alkyllithium followed by addition of D_3 as the second monomer.[11] Zilliox et al. used a similar approach involving initiation of D_3 by alkyllithium in a benzene/THF mixture.[11] In these cases molecular weight distributions were not reported but may be assumed to be wide since initiation of D_3 by living PSLi is slow. Furthermore, side reactions will occur, such as hydride elimination from PSLi[12] and ring-chain equilibria involving the propagating silanolate anions.

We have reported the synthesis of well-defined and narrow molecular weight distribution PMMA−PDMS block copolymers by initiation of MMA by an acetal-functionalized alkyllithium followed by acid-catalyzed hydrolysis and titration of the resulting alcohol with triphenyllithium followed by addition of D_3.[4,13−15] An alternative method for the synthesis of PMMA block copolymers has been reported involving the addition of benzaldhyde to the PMMA anion to give the corresponding lithium alcoholate followed by addition of ethylene oxide and similar monomers.[16] The redistribution of silanolate anions by chain transfer or by backbiting[17] can be suppressed in the presence of Li counterion and suitable promoters.[18,19]

Here we report the synthesis of P2VP−PDMS, P2VP−PDMS−P2VP, P4VP−PDMS, and P4VP−PDMS−P4VP block copolymers using methods similar to that developed earlier for the synthesis of PMMA-*b*-PDMS[4,13−15] as well as two more convenient methods for the synthesis of P2VP−PDMS block copolymers. The target block copolymers like PS−PDMS[20] and PMMA-*b*-PDMS block copolymers[4,13−15] are of interest as thermoplastic elastomers. Like the poly(vinylpyridine) homopolymers, they are also of interest as polybases that are expected to complex cooperatively with relatively weak polymeric proton donors such as poly(acrylic acid) or poly(vinylphenol) (PVPh). Whereas the more acidic poly(acrylic

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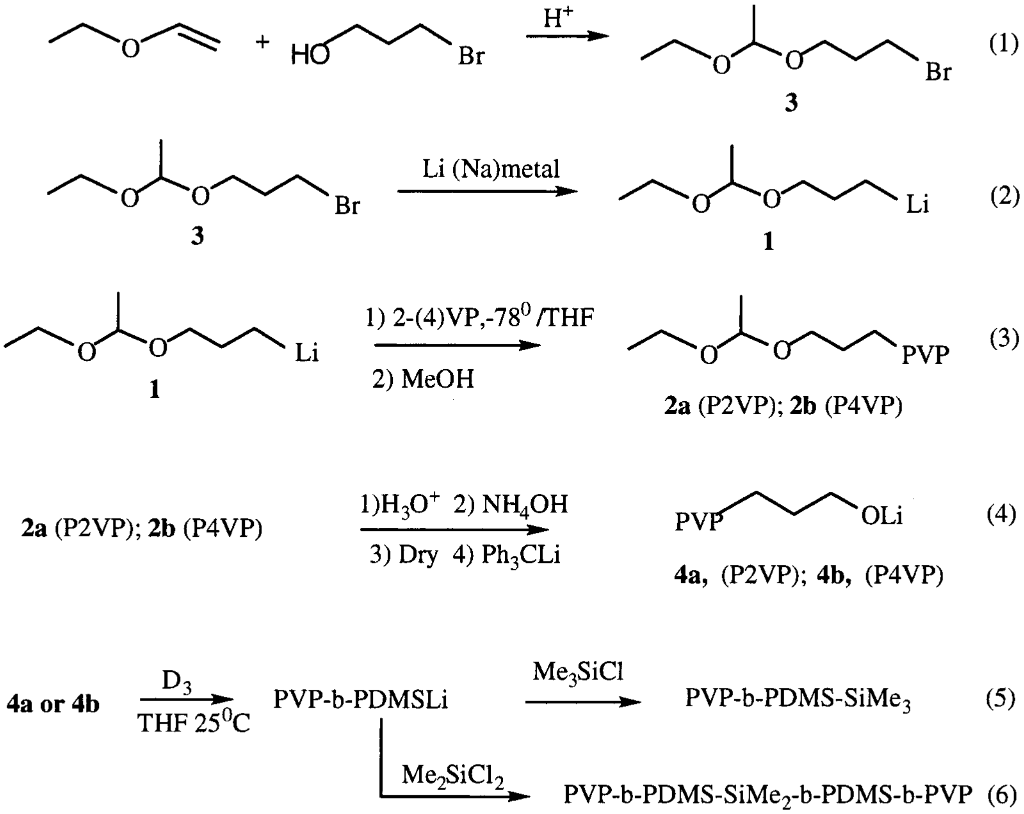
Scheme 1. Synthesis of PVP−PDMS Block Copolymers Using Initiator 1



acid) (PAA) will protonate P2VP or P4VP giving polyelectrolyte complexes,[21−23] PVPh, due to its much lower acidity, is expected to only hydrogen bond.[24,25]

Depending on molecular weights and stoichiometry, the PAA/PVP−PDMS or PVPh/PVP−PDMS block copolymer mixtures in solution are expected to self-assemble into graft, star, or network triblock copolymers, and this self-assembly process makes PVP−PDMS block copolymers attractive as a synthetic target.

Experimental Section

Reagents. Hexamethylcyclotrisiloxane (D_3), dimethyldichlorosilane (Me_2SiCl_2), trimethylchlorosilane (Me_3SiCl), and ethylene oxide (EO) (all purchased from Aldrich) were dried twice over CaH_2 and vacuum-distilled into ampules. Tetrahydrofuran (THF) was distilled as needed through the vacuum line from blue solutions of Na/K alloy. The 2- or 4-vinylpyridine and 2-isopropenylpyridine (2-IPP) monomers were distilled from CaH_2 and were purified further by stirring over a potassium mirror followed by vacuum distillation into ampules that were stored at −20 °C.

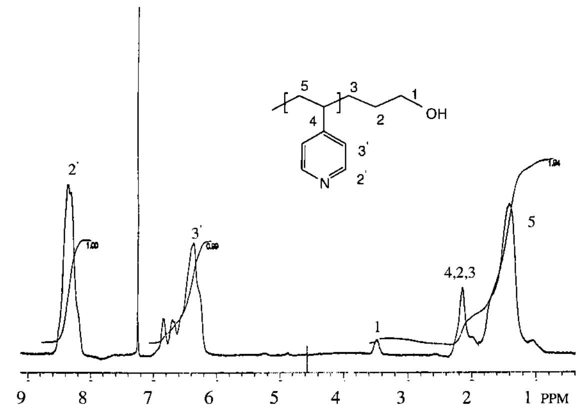
The synthesis of functionalized acetal initiator **1** (Scheme 1**,** eqs 1 and 2) and the corresponding alkyl bromide, **7**, were carried out as reported previously.[4,13−15] Thus, ethyl-3-lithiopropyl acetaldehyde acetal (**7**) was prepared following Eaton's method.[26] The synthesis of 2-isopropenylpyridine was carried out by the dehydration of the 2-(2-pyridyl)propanol catalyzed by concentrated sulfuric acid as described previously.[27]

Polymerizations. All polymerizations were carried out in a glass apparatus under high vacuum (10^{-5}−10^{-6} Torr) using break-seal methods. Narrow distribution P2VP or P4VP was prepared in THF at −78 °C by initiation of 1−3 g of 2-VP or 4-VP with acetal initiator **1** or with *t*-BuLi. Over a period of about 1.5 h the 2-VP or 4-VP monomer was vacuum-distilled into a vigorously stirred initiator solution kept at −78 °C. After termination with methanol or with **7** (Scheme 1), the acetal functionalized P2VP or P4VP was hydrolyzed in 25 mL of HCl (1.0 M) at room temperature for 3 h and then neutralized with ammonium hydroxide and isolated by filtration (Scheme 1, eq 5). The hydroxyl end-functionalized polymers (P2(4)VP−OH) were again dissolved in THF, precipitated in excess hexane, and dried in a vacuum oven at 60 °C for at least 3 days. Yields were quantitative. Titration of the P2(4)VP−OH with triphenylmethyllithium (TPML) in THF at 25 °C gave P2VP−OLi or P4VP−OLi (Scheme 1, eq 5). The TPML acts both as a base and indicator and does not react with PVP or D_3. The polymerization of D_3 (2−5 g) at a concentration between 1.0 and 2.0 M was initiated by P2VP−ROLi and was monitored by withdrawing aliquots during the course of polymerization followed by direct SEC analysis of these reaction solutions. Synthesis of the AB or ABA block copolymers was carried out by slow distillation of Me_3SiCl (Scheme 1, eq 5) or Me_2SiCl_2 (eq 6), respectively, into a rapidly stirred solution of P2(4)VP-*b*-PDMSLi. The progress of the coupling reaction with Me_2SiCl_2 was also monitored by direct sampling and analysis by SEC. The copolymers were obtained by precipitation into excess methanol. The precipitated copolymers were washed with methanol and dried for 72 h at 60 °C.

Characterization. *SEC analysis* was performed on a "Waters" model 510 HPLC pump, a U6K injector, a "Waters" 2 μm precolumn filter, and 500 and 10^4 Å "Ultrastyragel" columns using a "Waters" model 410 refractive index detector, a "Waters" model 484 UV/vis detector, a liquid flow meter, and a PC interface for data collection. The linear range of separation of the two (10 μm) columns was from M_n = 500 to 50 000 for the 500 Å column and M_n = 40 000−500 000 for the 10^4 Å column.

Calibrations were carried out with polystyrene (PS), P2VP (Polysciences), or PDMS standards (American Polymer Standards). SEC analysis of the P4VP precursorswas carried in THF containing 10 vol % methanol and 5 vol % triethylamine as the eluting solvent. THF containing 5 vol % triethylamine was used for analysis of the P2VP precursors. This method is simpler to use than that reported by Eisenberg and co-workers (*N*-methyl-2-pyrrolidinone at 90 °C as elution solvent).[28]

The molecular weights of the PVP−PDMS block copolymers were determined in toluene with polystyrene standards using



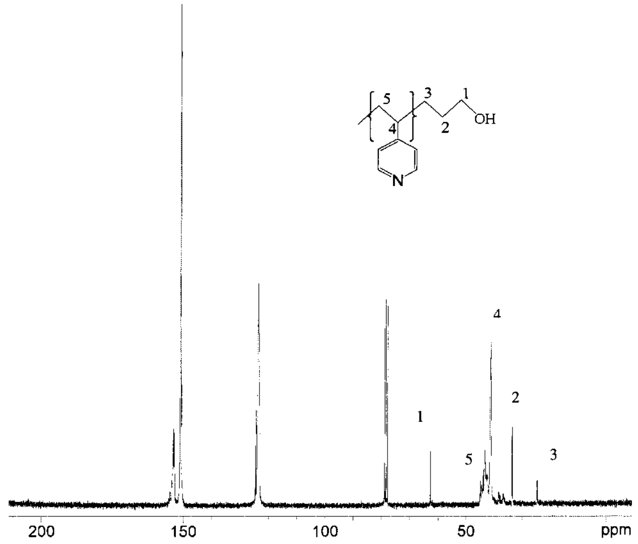


Figure 1. (a, top) Proton NMR (250 MHz) spectrum of P4VP−OH in $CDCl_3$ (Table 2). (b, bottom) Carbon NMR (250 MHz) spectrum of P4VP−OH in $CDCl_3$ (Table 2).

the universal calibration method to establish the PDMS calibration curve using the Mark−Houwink viscosity data from the literature.[29,30] We assume that the block copolymers containing relatively small P2(4)VP blocks closely resemble PDMS. In some cases these values were also checked using PDMS standards.

Proton and ^{13}C NMR measurements were performed on a Bruker model AM-250 MHz FT-NMR. The ^1H NMR analyses were carried out with 5 wt % solutions in $CDCl_3$ while the ^{13}C NMR were obtained with 10−15 wt % solutions. The SEC molecular weights of the PVP precursors were checked in some cases by ^1H NMR through integration of the initiator *tert*-butyl or acetal protons relative to the 6-pyridyl proton (Figure 1a) or by integration of methylene protons of the acetal initiator vs integration of the 6-pyridyl proton.

Results and Discussion

Synthesis of P2VP−PDMS and P4VP−PDMS Block Copolymers through Initiation with Lithioalkyl Acetals. The synthesis of narrow distribution acetal end-functionalized polyvinylpyridines involves the polymerization of 2-VP or 4-VP initiated by **1** followed by protonation (Scheme 1, eqs 1−3) (Tables 1 and 2). This was followed by the acid hydrolysis of the initiator acetal group (eq 4). As shown in Figure 1a, the proton spectrum of the protonated P4VP (**2a**) shows the expected two broad resonances corresponding to the 2-, 6-, and 3-,5- aromatic protons. Judging by the bandwidths and by the integration values, the two resonances at 6.70 and 6.85 ppm are not due to solvent impurities and are probably attributable to stereochemical fine structure of the 5-protons. The resonance of the 1-methylene protons of the initiator, **1**, is clearly visible at 3.50 ppm as are the 2- and 3-methylene protons at 2.0−2.2 ppm.

Table 1. Synthesis of Narrow MW Distribution P2VP-*b*-PDMS and Matching P2VP-*b*-PDMS−P2VP Copolymers (Scheme 1)[a]

	P2VP		P2VP-*b*-PDMS		P2VP−PDMS−P2VP		
no.	M_n[c]	M_w/M_n[c]	M_n[b]	M_w/M_n[b]	M_n[b]	M_w/M_n[b]	conv $D_{3\%}$
23	6200	1.06	9 500	1.12			5.0
24	5500	1.07	46 000	1.07			30
25	5500	1.07			96 000	1.09	30
26	1000	1.09	30 000	1.06			20
27	1000	1.09			53 000	1.10	20
28	1000	1.09	24 000	1.02			18
29	1000	1.09			47 000	1.10	18

[a] [PVP−OLi] from 0.001 to 0.002 M. [D_3] from 1 to 2.0 M. [b] SEC values calculated from universal calibration based on PS standards in toluene.[29,30] [c] Determined by SEC in THF.

Table 2. Synthesis of Narrow Distribution P4VP−PDMS Block Copolymers (Scheme 1)[a,b]

sample	M_n	M_w	M_w/M_n	D_3 conv (%)	[η] (dL/g)[g]
P4VP−acetal	900[c]	980	1.08		
P4VP−OH	810[c] 890[d]	880	1.08		
P4VP−PDMS					
17	91 000	97 000	1.07	40	
18	25 000	34 000	1.36[f]	18	
19	160 000 160 000[e]	167 000 167 000	1.03	52	0.66
20	32 000 37 000[e]	37 000 39 000	1.15	15	
21	58 000	67 000	1.16		
22	160 000	22 000	1.39[f]	60	

[a] [PVP−OLi] from 0.001 to 0.002 M. [D_3] from 1 to 2.0 M. [b] SEC values calculated from universal calibration based on PS standards in toluene. [c] Determined by SEC based on P2VP standards. [d] Determined by proton NMR through integration of 6-proton of pyridine and the *tert*-butyl group of initiator. [e] Determined by SEC used PDMS standards in toluene. [f] Reaction temperature at 45 °C. [g] Determined in THF.

The carbon NMR of the hydroxyl end-functionalized P4VP (Table 2) shows methylene carbons 1, 2, and 3 at 62.5, 33.8, and 24.0 ppm, respectively (Figure 1b). The complete hydrolysis of the acetal is also indicated by the absence of the resonance at 102 ppm corresponding to the acetal methine carbon. Hydrolysis of the acetal end group could be observed qualitatively by a slight decrease in apparent SEC MW.

Both P2VP− and P4VP−lithium alkoxides, **4a** and **4b**, respectively, are effective initiators of D_3 in contrast to Ph_3CLi or polystyryllithium or P2VPLi, and this is undoubtedly due to the greater O−Si bond strength (O−Si bond of 452 kJ/mol as compared to Si−C bond of 318 kJ/mol).[31] However, initially there were problems with the control of MW and MW distribution probably resulting form lithium silanolate exchange reactions.[19] Others have shown that the anionic polymerization of D_3 give narrow PDMS distributions with monofunctional lithium initiators only under certain conditions such as low degree of polymerization (DP), low initiator concentrations, and short polymerization times.[18a] At higher momomer conversions bimodal distributions were observed, and this was attributed to lithium silanolate aggregation.

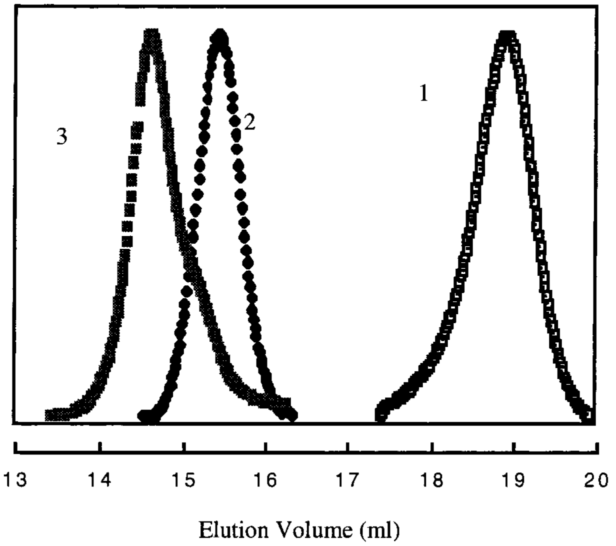


Figure 2. SEC chromatograms of P2VP−OH in THF (curve 1), P2VP−PDMS (curve 2), and P2VP−PDMS−P2VP in toluene (curve 3) (Table 1, no. 29).

As shown in Tables 1 and 2, we have found that the polymerization of D_3 in THF using high monomer concentrations ($1.0 < [D_3] < 2.0$ M) and relatively low monomer conversions (<40%) gave good control of MW, narrow MW distributions, and high PDMS block MW's. The P2VP−PDMS block copolymers have P2VP blocks with masses from 1000 to 6200 and block copolymer masses between 9500 and 96 000. The MW distributions are quite narrow, being between 1.02 and 1.12. Synthesis of the matching AB and ABA P2VP−PDMS−P2VP block copolymers having identical block compositions was carried out by reaction of the same P2VP−PDMSLi lithium silanolate solution with Me_3SiCl and Me_2SiCl_2, respectively.

The coupling of the lithium silanolate copolymers with Me_2SiCl_2 was especially challenging but was eventually successfully controlled by slow distillation of Me_2SiCl_2 into the rapidly stirred P2VP−PDMSLi solution (eq 6). The progress of the coupling reactions was followed by direct SEC analysis of the PVP−PDMSLi lithium silanolates.

As shown in Table 1, the triblock copolymers were approximately double the size of the corresponding AB copolymer, indicating successful coupling. It should be stressed that the above type synthesis has the advantage that a series of block copolymers may be prepared with the same PVP block and varying PDMS blocks.

A small low MW shoulder was visible in some instances, as shown in Figure 2. This shoulder most likely corresponds to an inadvertent excess of Me_2SiCl_2, resulting in the formation of uncoupled product and not to precursor, P2VP−PDMSLi, since it does not disappear on further addition of Me_2SiCl_2.

The acetal initiator route (Scheme 1) also proved efficient for synthesis of P4VP-*b*-PDMS (Table 2). The MW of the P4VP precursor was kept low since, at least in THF, P4VP becomes insoluble above a degree of polymerization of about 20.[33] The M_n of the P4VP-block copolymers ranged from 25 000 to 160 000. Again, the control of MW of the P4VP−PDMS block copolymers proved to be excellent, and the MW distributions were narrow in some cases even at very high MW's (Table 2, nos. 17 and 19). At a reaction temperature of 45 °C the MW distributions widened presumably as a result of increased silanolate redistribution reactions.[18]

Table 3. Synthesis of Narrow Distribution *t*-Bu-P2VP-*b*-PDMS Copolymers through End-Functionalization of P2VPLi with Bromoacetal, 3 (Scheme 2)[a,b]

sample	M_n[b]	M_w[b]	M_w/M_n[b]	D_3 conv (%)	[η] (dL/g)[f]
P2VP−acetal	2300[c]	2460	1.07		
P2VP−OH	2200[c] 2300[d]	2300	1.07		
P2VP−PDMS					
1	34 000	37 000	1.08	15	
2	37 000	40 000	1.09	19	
	40 000[e]	42 000			
3	61 000	69 000	1.14	29	
4	66 000	74 000	1.10	31	
5	67 000	73 000	1.09	34	0.36
6	67 000	72 000	1.08	32	
7	89 000	113 000	1.27	45	
8	140 000	170 000	1.29	70	0.66
	150 000[e]	180 000			
9	260 000	330 000	1.28	82	

[a] [PVP−OLi] ranges from 0.001 to 0.002 M. $[D_3]_0$ ranges from 1 to 2.0 M. [b] SEC values calculated from universal calibration based on PS standards in toluene. [c] Determined by SEC based on P2VP standards [d] Determined by ^1H NMR by integration of 6-proton of pyridine and the *tert*-butyl group of initiator. [e] Determined by SEC used PDMS standards in toluene. [f] Determined in THF.

Table 4. Synthesis of Narrow Distribution *t*-Bu-P2VP-*b*-PDMS Copolymers through End-Functionalization of P2VPLi with Bromoacetal, 3 (Scheme 2)[a,b]

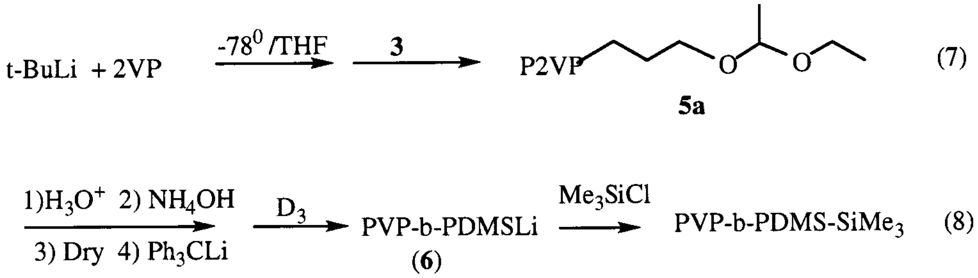
sample	M_n	M_w	M_w/M_n	conv D_3 (%)[d]	[η] (dL/g)[e]
P2VP−acetal	900[c]	1030	1.15		
P2VP−OH	800[c] 900[d]	900	1.12		
P2VP−PDMS					
10	10 000	10 400	1.04	5	
11	48 000	52 000	1.08	24	0.27
12	42 000	50 000	1.19	20	
13	67 000	80 000	1.20	32	
14	110 000	120 000	1.09	50	
15	156 000	164 000	1.05	50	0.66
16	290 000	360 000	1.25	80	1.20

[a] [PVP−OLi] ranges from 0.001 to 0.002 M. $[D_3]_0$ ranges from 1 to 2.0 M. [b] SEC values calculated from universal calibration based on PS standards in toluene. [c] Determined by SEC based on P2VP standards. [d] Determined by ^1H NMR by integration of 6-proton of pyridine and the *tert*-butyl group of initiator. [e] Determined in THF.

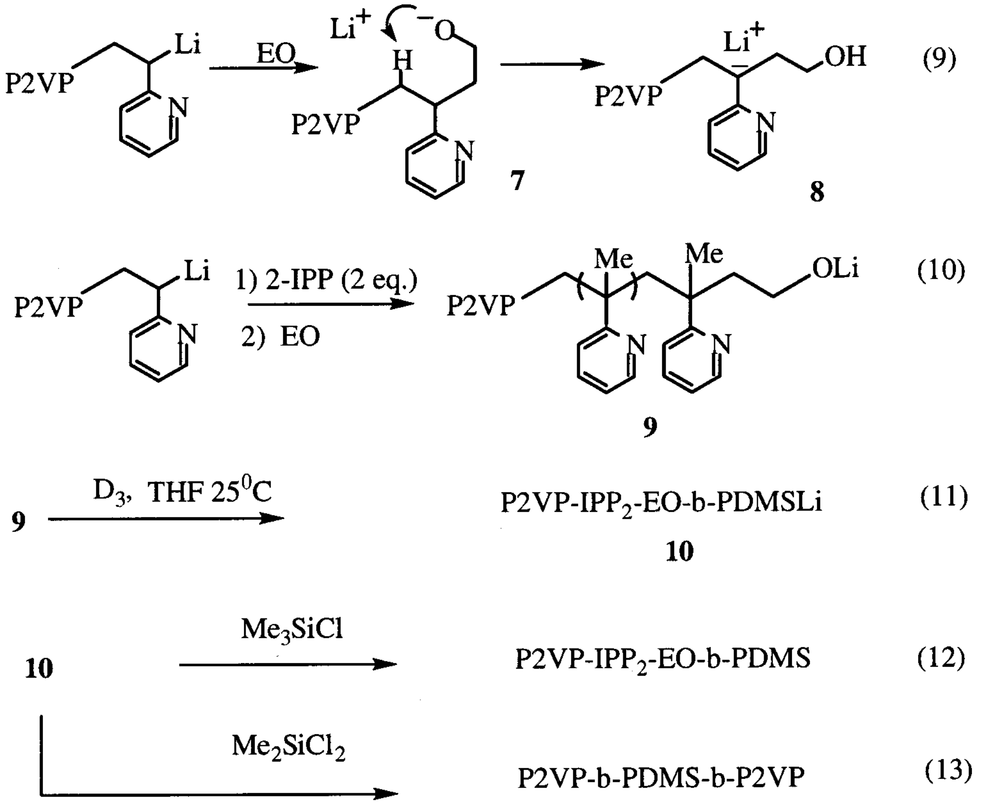
We also found that size exclusion chromatography of P4VP and/or the P4VP-*b*-PDMS copolymers (presumably other P4VP block copolymers as well) may be carried out conveniently at ambient temperatures by using THF containing 10 vol % methanol and 5 wt % triethylamine. However, SEC analysis was generally carried out in toluene because of the extremely small refractive index increment of PDMS in THF.

Synthesis of P2VP−PDMS Copolymers through End-Functionalization with Bromoalkyl Acetals. The functionalization achieved by terminating the P2VP anion with bromoacetal **3** (Scheme 2, eq 7) is more convenient synthetically in the sense that the lithiation step is avoided. The MW distributions of the resulting acetal functionalized P2VP's determined by SEC were found to be narrow (Tables 3 and 4). The acetal hydrolysis could be observed by SEC as a slight decrease

Scheme 2. Synthesis of P2VP–PDMS Block Copolymers Using Alkylation of P2VPLi with Bromoacetal, 3



Scheme 3. Formation of P2VP–PDMS Block Copolymers by End-Functionalization of P2VPLi with 2-Isopropylphenylpyridine and Ethylene Oxide



in apparent MW. The corresponding end-functionalization of P4VP with bromoacetal **3** was found to be unsuitable presumably because of the lower reactivity of the P4VP anion that may be hampered further by the alkylation of the pyridine nitrogen with the bromoacetal. Apparently, this latter reaction did not interfere in the case of P2VP.

Titration of the P2VP precursors alcohols with triphenylmethyllithium (Scheme 2, eq 8) affords the end-functionalized P2VP lithium alkoxides **6** that rapidly initiate D_3 to give relatively narrow molecular weight distribution lithium silanolate end-functionalized PVP–PDMS block copolymers.

Tables 3 and 4 list the P2VP–PDMS block copolymers made using the bromoacetal terminator pathway using P2VP–OH precursors with M_n's of 2200 and 800, respectively. By this method also a series of P2VP–PDMS block copolymers may be obtained with the same P2VP chain length and varying PDMS block lengths. This makes it possible to evaluate the role of the PDMS block in a number of associative processes.

Molecular weights were cross-checked in some cases by proton NMR or by SEC methods using PDMS standards and were found to be in excellent agreement (Tables 3, no. 8). The masses (M_n) of the P2VP–PDMS block copolymers were between 10 000 and 290 000 with polydispersity indices between 1.04 and 1.29. The higher PDMS molecular weights typically required longer reaction times, and thus side reactions were expressed through wider MW distributions. Nevertheless, for number-average molecular weights below about 100 000 polydispersities were generally close to about 1.10. In some cases excellent polydispersities could be obtained even at relatively high MW and D_3 conversions (Table 4, nos. 14 and 15).

Synthesis of P2VP-*b*-PDMS through End-Capping with Ethylene Oxide. The above synthetic methods require the rather tedious synthesis of the bromoacetal **3** and the corresponding lithio derivative (Scheme 1). An attempt to synthesize P2VP–PDMS block copolymers more directly by sequential anionic polymerization via the capping of P2VP anion with ethylene oxide failed (Scheme 3). A P2VP-*b*-PDMS copolymer with a bimodal distribution was obtained with a M_w/M_n of 1.55 (Table 4, **1b**). Upon addition of ethylene oxide to the living P2VP anion solution, some

Table 5. P2VP−PDMS Copolymers (Scheme 3, Eqs 10−13)[a,b]

sample	M_n	M_w	M_w/M_n	conv of D_3 (%)
1a. P2VP−EO[c]	1500	1800	1.19	
1b. P2VP−EO−PDMS	2200	3500	1.55	2
2a. PIPP−EO[c]	1600	1700	1.05	
2b. PIPP−PDMS	7140	9000	1.26	10
2c. PIPP−PDMS−PIPP	12700	15400	1.21	10
3a. P2VP−IPP−EO[c]	6300	7400	1.18	
3b. P2VP−IPP−EO−PDMS	13700	17000	1.20	16

[a] [PVP−OLi] ranges from 0.001 to 0.002 M. $[D_3]_0$ ranges from 0.5 to 1.0 M. [b] SEC values calculated from universal calibration based on PS standards in toluene. [c] Determined by SEC based on P2VP standards.

of the red color of the P2VPLi disappeared right away, but a faint reddish color persisted even at reaction temperatures as high as 0 °C. Apparently only a portion of the picolyl anions was converted to lithium alcoholate since addition of D_3 gave a low molecular shoulder attributable to the P2VP precursor anion that is a poor initiator of D_3. A possible side reaction involving the formation of picolyl carbanion **8** from the alkoxide **7** and accounting for both observations is shown in Scheme 3. The basicity of the carbanion **8** is too low to initiate D_3, and this is consistent with the poor D_3 initiating ability of benzyl and picolyl carbanions referred to in the Introduction. The intramolecular deprotonation of the methine proton of the pyridine end unit occurring through a six-membered transition state (Scheme 3) is expected to be favored entropically and is reasonable given the high basicity of lithium alkoxides in ethers.[5] A similar reaction has been described by Boileau et al. for the reaction of the fluorenyl anion with EO.[32] The above interpretation was confirmed by our being able to avoid the deprotonation reaction by capping of the P2VP chain end anion with 1−2 equiv/chain of 2-isopropenylpyridine (2-IPP) that lacks an α-hydrogen. (With 1 equiv of 2-IPP, deprotonation may still occur through a seven-membered ring.) The 2-IPP end-capped P2VP reacted quantitatively with ethylene oxide as indicated by the lack of any residual color attributable to the formation of a picolyl anion. The formation of a narrow MWD block copolymer indicated that the resulting alkoxide anion **9** quantitatively initiates D_3 to give the P2VP−PDMS block copolymers **2b** and **3b** from the corresponding precursor anions (Table 5). The formation of P2VP-*b*-PDMS-*b*-P2VP by coupling with dichlorodimethylsilane is also possible. Hence, this method provides a third route for the synthesis of P2VP−PDMS block copolymers (Scheme 3). End-capping of P4VPLi with 2-IPP was unsuccessful. Finally, SEC analysis indicates that the PVP−PDMS block copolymers are stable at ambient conditions either in solution or as solids, indicating that the Si−O−C bonds connecting the PDMS to the PVP block do not readily hydrolyze. This would not be expected to be the case for a more acidic environment for instance for the case of copolymers of PVP and poly(acrylic acid).

Conclusions

The anionic synthesis is described of narrow distribution P2(4)VP−PDMS and P2VP−PDMS−P2VP block copolymers by two methods involving the use of lithium initiators (method 1) or the corresponding acetal-functionalized alkylating agents (method 2). Upon deprotection of the initiator acetal group the P2VP- or P4VP-bound hydroxyl groups are converted to the lithium alkoxides that initiate D_3 to give the living block P2(4)VP-*b*-PDMSLi copolymers that may be terminated or coupled to produce AB or ABA block copolymer of the same composition. The use of high D_3 concentrations combined with lower D_3 conversions was shown to be essential in minimizing the occurrence of backbiting and other side reactions that tended to broaden the MW distributions of the PDMS block.

The P2VP−PDMS block copolymers could also be prepared by end-capping of the P2VPLi with 2-IPP followed by addition of ethylene oxide and D_3. The PVP-*b*-PDMS block copolymers do not show hydrolysis of the Si−O−C bond upon standing. However, the above synthetic procedures are not applicable for the synthesis of poly(acrylic acid)-*b*-PDMS and similar block copolymers.

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