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Synthesis and Self-Assembly of Diblock Copolymers through Hydrogen Bonding. Semiquantitative Determination of Binding Constants

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ABSTRACT: The synthesis of poly(4-vinylpyridine) block copolymers containing a poly(4-(4-(4-fluorophenyl)sulfonylphenyl)sulfonyl-4′-*N*-ethyl-*N*-2-(4-hydroxyphenolic)ethylazobenzene) (PNLO) segment with a MW between 7300 and 19 300 was carried out by the reaction of the 4-fluorophenyl end group of the PNLO segment with a low molecular weight (DP = 33 or less) phenol end-functionalized P4VP under basic conditions. Self-assembly of this diblock copolymer occurs with polystyrene-*b*-poly(vinylphenol) (PS-*b*-PVPh) or PMMA-*b*-poly(2-hydroxyethyl methacrylate) (PMMA-*b*-PHEMA) block copolymers, having short H-bond donor blocks, through the formation of H-bonds with the acceptor P4VP blocks. This process was studied by the increased solubility of the P4VP-*b*-PNLO copolymer in toluene/CH_2Cl_2 (99/1, v/v) or in ethyl acetate due to the formation of the more soluble block copolymer complexes. The increases in solubility were monitored by visible absorption at about 456 nm, the absorption maximum of the PNLO segment. The apparent binding constants to the PS-*b*-PVPh and the PHEMA-*b*-PMMA block copolymers in toluene/CH_2Cl_2 (99/1, v/v) and in ethyl acetate were on the order of 10^5 and 10^3 M^{-1}, respectively.

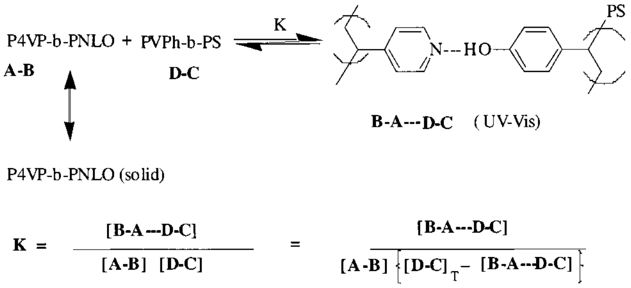
Introduction

The synthesis and self-assembly of block copolymers through phase separation of the blocks into separate domains are well documented.[1−7] Such block copolymers typically are synthesized through sequential chain polymerization of vinyl or cyclic monomers in which the blocks are connected through covalent bonds.[8−10] However, there have been relatively few reports of syntheses of block copolymers formed spontaneously through noncovalent interactions, i.e., ionic or H-bonding, of one or more of the blocks.[9−13]

We report here the synthesis and solution self-assembly of AB and CD block copolymers containing short H-bond donor, D, and acceptor, A, blocks (Scheme 1). The choice of this type of interaction, in addition to synthetic convenience, was motivated by the desired absence in the formed copolymers of ions and consequently ionic interactions that could complicate analysis of the self-assembled polymer system. A further consideration in the design of these block copolymers was the inclusion of polymeric chromophores into either the AB or CD blocks that could facilitate the study of the solution assembly process through UV/vis spectroscopy. For instance, the solubility, or lack thereof, of one of the blocks and the increase or decrease upon complex formation could easily be checked spectroscopically.

In the following we report the synthesis of AB and CD type block copolymers capable of mutual interaction through short blocks of poly(vinylphenol) (PVPh) or poly(2-hydroxyethyl methacrylate) (PHEMA) as H-bond donors (D).[14] A short poly(4-vinylpyridine) (P4VP) (A) attached to a polymeric B block containing azo chromophores in the backbone serves as the H-bond acceptor. The choice of the "inert" C block was made with regard to both synthetic convenience and solubility characteristics. For the case of the PVPh block copolymers, polystyrene was chosen as the C block. For the case of the HEMA block copolymers the C block was selected to be PMMA. The relative acidities of the protonated 4-pyridine and 2-hydroxyethyl or phenol groups predict strong H-bonding (between 3 and 6 kcal/mol[15]) without significant proton transfer, and this is confirmed by several studies.[16−18] Thus, the formation of cooperative and strong interactions between relatively short A and D blocks is anticipated.

Scheme 1. Formation of "Tetrablock" Copolymer Assemblies by Hydrogen Bonding between the PVPh (D) and the P4VP (A) Blocks



Both PVPh and PHEMA are readily accessible through anionic polymerization of the corresponding protected *p*-(*tert*-butyldimethylsiloxy)styrene (TBDMSS)[19] or 2-(*tert*-butyldimethylsiloxyethyl) methacrylate (BDMSEMA)[20] monomers. The choice of P4VP rather than the more easily polymerizable P2VP was motivated by the formation of stronger H-bonds for P4VP.[21] The low MW (DP < 40) narrow MW distribution P4VP block is subject to convenient anionic polymerization of the unprotected 4-vinylpyridine (4VP).[22,23] Thus, although the polymerization of 4-VP under synthetically convenient conditions is restricted to relatively low degrees of polymerization (DP < 40), this is not a problem in this case.

Results and Discussion

Polymerizations and End-Functionalization. The molecular weight distributions obtained by the 3,3-dimethyl-1,1-diphenyl-1-lithiobutane (DMPLB)-initiated

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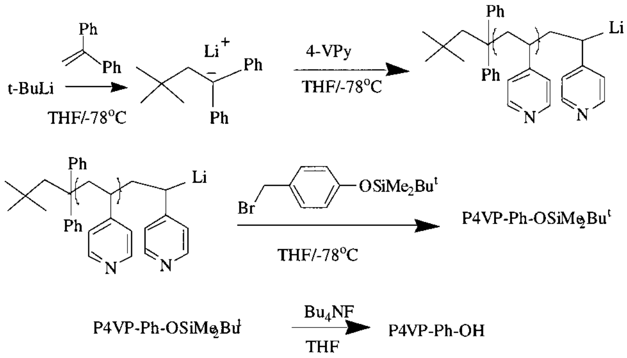
Table 1. Synthesis and Characterization of P4VP-*b*-PNLO

P4VP−PhOH[a]		P4VP-*b*-PNLO[a]		
sample no.	M_n/MWD	sample no.	M_n	M_w/M_n
1	1150/1.16	**6**	15 800	1.40
1	1150/1.16	**9**	11 000	1.60
3	3300/1.25	**8**	17 000	2.00
4	1400/1.40			

[a] Determined by SEC using polystyrene standards.

Scheme 2. Synthesis of Phenol End-Functionalized P4VP



anionic polymerization of 4VP in THF at −78 °C were generally narrow (Table 1) with the exception of sample **4**, the MWD ($D = 1.40$) of which was broadened by a too rapid addition of monomer leading to polymer precipitation. Nevertheless, a number-average molecular weight as high as 3300 could be prepared without significant broadening (Table 1, sample **3**).

The synthesis of several phenol end-functionalized poly(4-vinylpyridine)'s (P4VP−Ph−OH) was carried out by the reaction of living P4VPLi in THF at −78 °C with 4-*tert*-butyldimethylsiloxybromomethylbenzene (BDMBB) prepared in turn by the free radical bromination of *tert*-butyldimethylsiloxytoluene (BDMST) (Scheme 2).[24,25] After addition of BDMST the characteristic orange-red color of the living P4VP disappeared, indicating the alkylation of the polymer anion. The ^{1}NMR of the BDMST end-capped P4VP shows the resonances at 0.1 and 0.9 ppm of the methyl and *tert*-butylsilyl groups as shown in Figure 1a. Upon reaction with tetrabutylammonium fluoride the peaks disappeared due to the cleavage of the TBDMS group, and there is a new peak at 4.90 ppm corresponding to the phenolic end group (Table 1, sample **1**, Figure 1b). The extent of the functionalization determined by proton NMR was calculated as about 85 ± 10% by integration of the resonances of the 2- and 6-protons of the pyridine group at 8.3 ppm relative to that of the phenolic −OH group.

P4VP-*b*-PNLO. An NLO active polymer containing main chain azo chromophores referred to as PNLO had been synthesized previously by the step polymerization of 4-(4-(4-fluorophenylsulfonyl)phenyl)sulfonyl-4′-*N*-ethyl-*N*-2-(4-hydroxyphenolic)ethylazobenzene (FSAB) in *N*,*N*-dimethylacetamide (DMAc) at 165 °C in the presence of potassium carbonate.[26] This step polymerization proceeds by the nucleophilic aromatic substitution of a 4-fluorophenyl group by potassium phenolate. The MW's of the homopolymers were varied between 2000 and 20 000. MW distributions as expected were relatively broad, but the polymer could be fractionated to give a MW distribution of about 2.0.

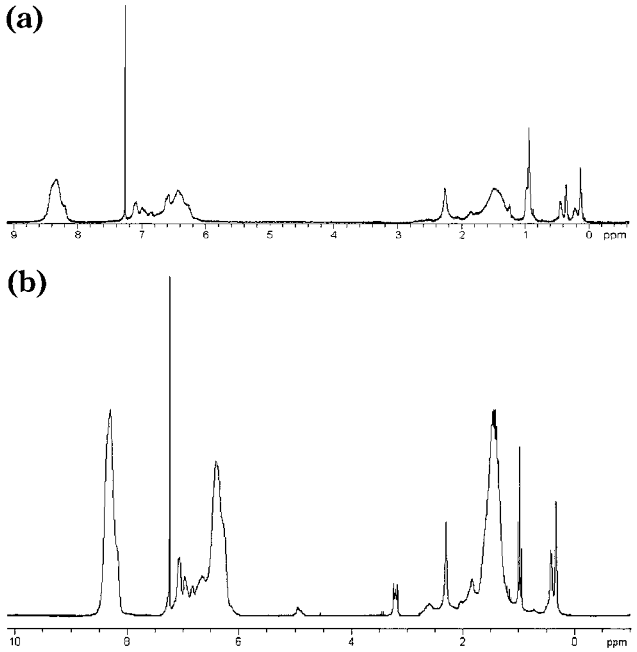


Figure 1. (a) Proton NMR 250 MHz spectrum of P4VP−Ph−OSiMe$_2$Bu^t (precursor of **1**) in CDCl$_3$ at 30 °C. (b) Proton NMR 250 MHz spectrum of P4VP−Ph−OH (**1**) in CDCl$_3$ at 30 °C.

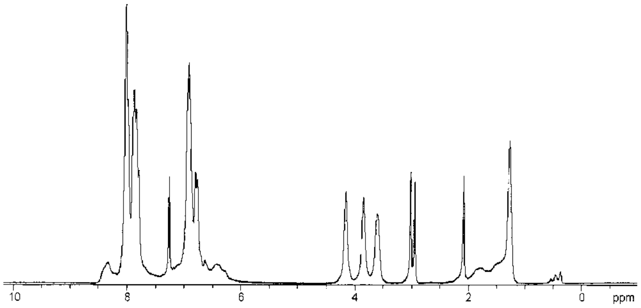
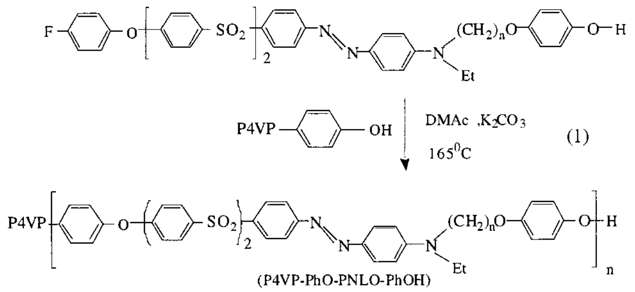


Figure 2. Proton NMR 250 MHz spectrum of P4VP−PNLO (**9**) in CDCl$_3$ at 30 °C.

Scheme 3. Synthesis of P4VP-*b*-PNLO



The P4VP-*b*-PNLO block copolymer was obtained by the reaction of P4VP−Ph−OH (Table 1, samples **6**, **8**, and **9**) with the FSAB in DMAc at 165 °C in the presence of potassium carbonate (Scheme 3). The step polymerization involves a nucleophilic aromatic substitution of fluoride by the potassium phenolate anion end group of the P4VP precursor. The block copolymer was isolated by precipitation into excess methanol, which is a good solvent for P4VP. Thus, no P4VP precursor could be seen in the SEC chromatogram of the P4VP-*b*-PNLO. In all cases a small low MW sideband was visible in the SEC chromatogram that was difficult to remove and may be due to a cyclic PNLO fraction. The NMR spectrum of the resulting block copolymer (P4VP-*b*-PNLO, sample **9**) is shown in Figure 2. The aromatic region consists of two broad bands centered at about

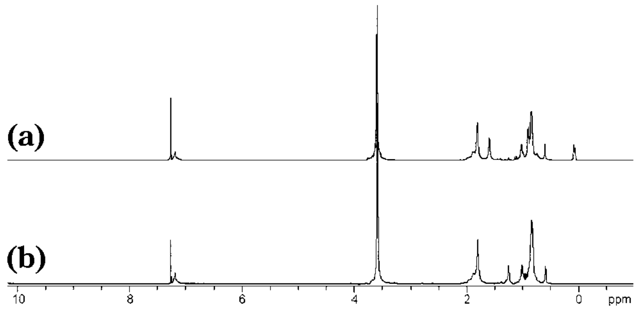
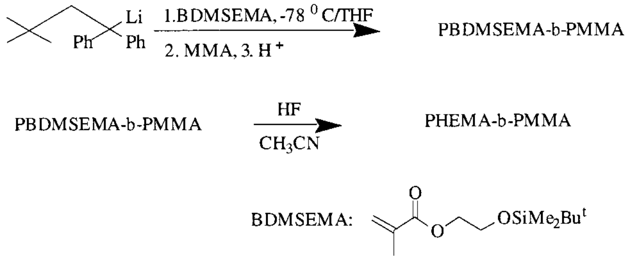


Figure 3. (a) Proton NMR 250 MHz spectrum of PMMA-*b*-PBDMSEMA (Table 2, sample **10**) in $CDCl_3$ at 30 °C. (b) Proton NMR 250 MHz spectrum of PMMA-*b*-PHEMA (Table 2, sample **11**) in $CDCl_3$ at 30 °C.

Scheme 4. Synthesis of PHEMA-*b*-PMMA



7.7−8.0 and 6.6−6.9 ppm, corresponding to the aromatic protons of the PNLO block. The resonances at 8.3 and 6.4 ppm are attributable to the 2-/6- and 3-/5-pyridine protons, respectively. The $-NCH_2CH_2O$, $-NCH_2CH_2O$, and $-NCH_2CH_3$ protons of the NLO repeat units are clearly visible at 4.2, 3.8, and 3.6 ppm, respectively, together with the corresponding $-NCH_2CH_3$ methyl group at 1.2 ppm. The methylene and methine protons of the P4VP block are visible between 1.3 and about 2 ppm. The resonances at 2.1 and 3.0 ppm are due to DMAc.

Upon addition of aqueous HCl acid (5%) to a solution of the resulting P4VP-*b*-PNLO block copolymer in CH_2Cl_2, the aqueous layer showed an intense red coloration of the PNLO segment, indicating partitioning of the block copolymer into the aqueous layer. Since the PNLO precursor homopolymer is completely insoluble in the aqueous acid, this indicates the protonation of the P4VP block and the subsequent partitioning of the now more water-soluble diblock copolymer into the acidic aqueous layer due to the excellent solubility of the poly(4-vinylpyridinium chloride) block in water.

PHEMA-*b*-PMMA. The synthesis and purification of 2-(*tert*-butyldimethylsiloxy)ethyl methacrylate) (BDMSEMA) were carried out following a reported procedure by Nakahama.[20] This block copolymer was obtained by the DMPLB-initiated polymerization of BDMSEMA in THF at −78 °C followed by the addition of MMA and termination by water or methanol (Scheme 4). After the deprotection of the TBDMS group with HF in CH_3CN, the proton resonances of the CH_3Si- peak near 0.1 ppm and of the $Si-C(CH_3)_3$ at 0.9 ppm of the precursor PBDMSEMA block cannot be observed (Figure 3).

PVPh−PS Block Copolymers. PVPh-*b*-PS was synthesized by the DMPLB initiated sequential anionic polymerization of BDMSS and styrene in THF at −78 °C (Scheme 5). The red coloration of the living PBDMSS and PS living polymers is virtually identical so that the transformation of the living PBDDMSS chain into PSLi could not be readily observed. However, the PBDMSS-*b*-PS block copolymers had narrow MW distributions (Table 3, samples **12** and **13**). The deprotection of the PBDMSS blocks with HCl was in excess of 95% as shown by NMR. Thus, upon reaction with HCl the resonances at 0.1 and 0.9 ppm corresponding to the TBDMS group disappeared completely as shown in Figure 4.

Table 2. Synthesis and Deprotection of PBDMSEMA-*b*-PMMA[a]

sample no.		PBDMSEMA	PBDMSEMA-*b*-PMMA	
		M_n	M_n	M_w/M_n
10	PBDMSEMA-*b*-PMMA	700	4200	1.08
11	PHEMA-*b*-PMMA	400	4100	1.09

[a] Determined by SEC using PMMA standards.

Because we were interested in the H-bonding to a P4VP-*b*-PNLO block copolymer in which the PVPh block was sandwhiched between two other blocks, we also synthesized a PS-*b*-PVPh-*b*-PS triblock copolymer. This polymer was synthesized by the lithium naphthalenide-initiated sequential anionic polymerization of BDMSS and styrene (Scheme 6, Table 3, sample **14**). The polydispersity of the PBDMSS precursor was reasonably narrow ($D = 1.22$), and the NMR analysis was in good agreement with the monomer/comonomer ratio. After termination with methanol, the PS−PBDMSS−PS triblock copolymer was deprotected by Bu_4NF to give the correponding PS-*b*-PVPh-*b*-PS copolymer (Table 3, sample **18**).

Although the MW distribution of the PS-*b*-PBDMSS-*b*-PS triblock copolymer was narrow as shown by SEC using THF as elution solvent, the chromatogram of the deprotected PS-*b*-PVPh-*b*-PS triblock copolymer showed a bimodal distribution and shorter elution volumes (Figure 5). Furthermore, the SEC chromatograms were concentration-dependent. These observations are consistent with the formation of intermolecular cooperative H-bonds between two or more PVPh segments, resulting in the formation of block copolymer dimers or trimers (Scheme 7). It is interesting that this interaction appears to occur in THF which is expected to be a good H-bond acceptor for PVPh. It is plausible that the long PVPh segment (MW is about 15 000) favors this entropically favored cooperative PVPh−PVPh interaction. This appears to be the first direct observation by SEC of complex formation between identical copolymer blocks through hydrogen bonding. Consistent with this interpretation, the PS-*b*-PVPh block copolymers, having relatively short PVPh chains, showed only one SEC peak, and the concentration effects observed with the triblock copolymer were absent.

Block Copolymer Self-Assembly. Although the formation of complexes between the P4VP and PVPh blocks by the formation of cooperative hydrogen bonding has been detected directly, for instance through IR spectroscopy, this method was not feasible for the current dilute solution systems.[12] However, some information could be obtained by the use of UV/vis spectroscopy. This is based on the lack of a visible absorption of the PS, PVPh and P4VP blocks at the PNLO absorption maximum of 456 nm. The very low solubility (about 10^{-7} M) of the P4VP-*b*-PNLO copolymers in toluene/CH_2Cl_2 (99/1, v/v), compared with the PS-*b*-PVPh block copolymers which are toluene-soluble, allows determination of the degree of complex formation.

Table 3. Synthesis and Deprotection of PBDMSS-*b*-PS Block Copolymers^a

	PS-*b*-PBDMSS				PS-*b*-PVPh	
sample no.	$M_n{}^b$ PBDMSS	M_n	M_w/M_n	sample no.	$M_n{}^c$ PS−PVPh	M_w/M_n
12	4 000	19 700	1.08	**16**	15 600−2100	1.10
13	10 300	32 100	1.09	**17**	17 800−5300	1.07
14	30 300	247 000	1.22	**18**^{e}	201 000−15 500	*d*

^{a} Determined by SEC using polystyrene standards in THF. ^{b} M_n of the PBDMSS block determined by ^{1}H NMR; M_n of PS block determined by subtracting M_n of PBDMSS from SEC determined M_n of the block copolymer. ^{c} M_n of PS blocks calculated from MW of PS-*b*-PVPh (SEC) and MW of PBDMSS (NMR). M_n of PVPh blocks calculated from M_n of PBDMSS. ^{d} Determination by SEC not possible; see text. ^{e} M_n of **18** calculated value from M_n of the PS-*b*-PBDMSS.

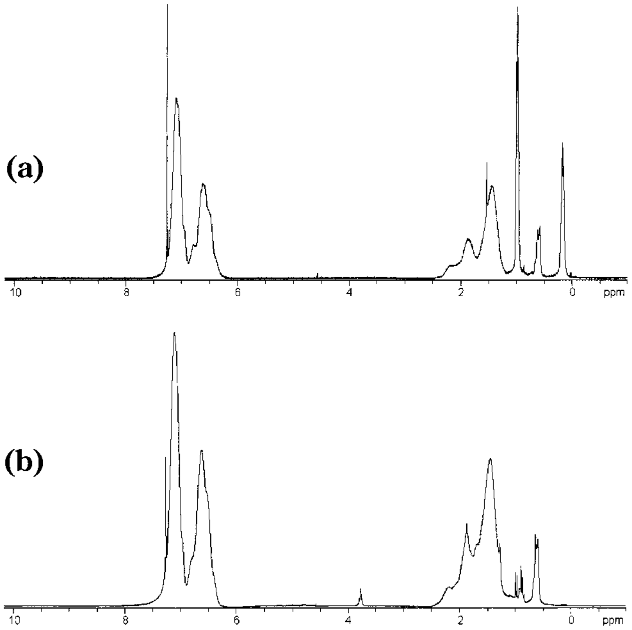
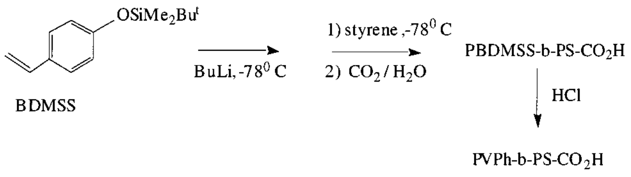
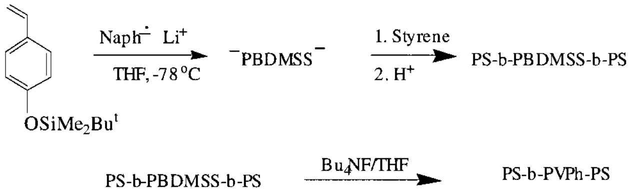


Figure 4. (a) Proton NMR 250 MHz spectrum of PS-*b*-PBDMSS (Table 3, sample **12**) in $CDCl_3$ at 30 °C. (b) Proton NMR 250 MHz spectrum of PS-*b*-PVPh in $CDCl_3$ (Table 3, sample **16**) at 30 °C.

Scheme 5. Synthesis of Poly(styrene-*b*-4-vinylphenol), PS-*b*-PVPh



Scheme 6. Synthesis of PS-*b*-PVPh-*b*-PS



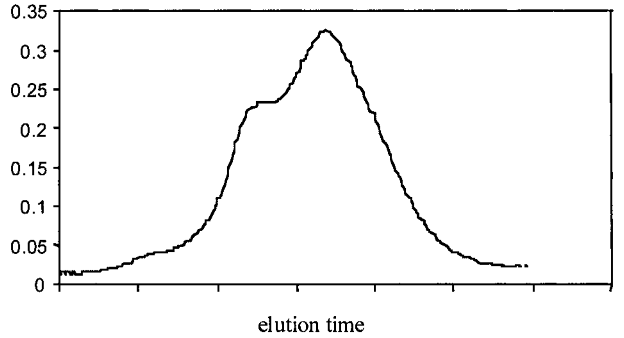
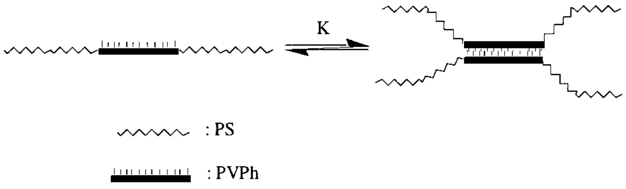


Figure 5. SEC chromatogram of PS-*b*-PVPh-*b*-PS (Table 3, sample **18**).

Scheme 7. Self-Association of PS-*b*-PVPh-*b*-PS by Hydrogen Bonding between Two PVPh Blocks in THF



As pointed in the Introduction and because of the reported pK_a values of the phenolic and hydroxyethyl groups in this case H-bonding is expected to occur rather than proton transfer.[27] This hydrogen-bonding is expected to form (PS-*b*-PVPh)$_n$···(P4VP-*b*-PNLO)$_m$ assemblies that would be expected to have a greater solubility in toluene compared with that of the P4VP-*b*-PNLO block copolymer given the greater solubility of the PS-*b*-PVPh block copolymer in the solvent mixture. Thus, upon addition of the PS-*b*-PVPh block copolymer to a suspension of the essentially undissolved P4VP-*b*-PNLO block copolymers in toluene/CH_2Cl_2 (99/1, v/v), the solutions became strongly colored consistent with the formation of a toluene-soluble, H-bond-mediated, BA−DC complex between the PVPh and P4VP blocks. The shape of the UV/vis spectrum and its absorption maximum were found to be unaffected by complex formation. Upon increasing the concentration of the PVPh-*b*-PS block copolymer, while keeping the total concentration of the P4VP-*b*-PNLO constant, the color of solutions intensified, and the UV/vis absorption of the PNLO at 456 nm increased consistent with increased complex formation. In all cases an excess of P4VP-*b*-PNLO solid was present.

The increased absorptivity of the BA−DC complex in the toluene/CH_2Cl_2 mixture was used to calculate its concentration. This in turn allowed calculation of apparent binding constants according to Scheme 1 in which [A−B] is the molar concentration of the uncomplexed P4VP-*b*-PNLO copolymer, [B−A···D−C] is the molar concentration of the block copolymer complex, and [C−D] is the molar concentration of the uncomplexed PVPh-*b*-PS copolymer.

The concentration of dissolved P4VP-*b*-PNLO is assumed to be equal to the saturation value of the various samples that were determined independently. We assume also that the P4VP-*b*-PNLO molar extinction coefficient determined in methylene chloride ($\epsilon = 6.75 \times 10^5$ for sample **8**) does not change from methylene chloride to toluene/CH_2Cl_2 and that the extinction coefficient of P4VP-*b*-PNLO is not affected by the formation of the complexes.

Table 4. Binding Constants of PVPh-*b*-PS[a] or PHEMA-*b*-PMMA[b] to P4VP-*b*-PNLO (8) and P4VP-*b*-PNLO (9) by UV/Vis Spectrometry in Toluene/CH_2Cl_2 (99/1, v/v)

polymers	M_w/M_n	[copol] ($\times10^7$ M)	[VPh] or [HEMA] ($\times10^5$ M)	K ($\times10^{-5}$ M^{-1})
16 + **8**	1.08	131	21.8	7.9
		610	101	7.8
17 + **8**	1.09	103	44	6.3
		35	15	5.0
18 + **8**	1.22	3.7	4.6	6.3
		2.2	2.8	4.5
11 + **8**	1.09	127	3.9	0.05
		280	8.6	0.04
16 + **9**	1.08	38	6.3	6.1
		73	12.2	9.2
17 + **9**	1.09	29	12	1.0

[a] Characterized by SEC based on polystyrene standards. [b] Based on PMMA standards.

The apparent binding constants of PS-*b*-PVPh copolymers **16**, **17**, and **18** to P4VP-*b*-PNLO (**8** and **9**) in toluene/CH_2Cl_2 (99/1, v/v) were calculated following Scheme 1 and range from 4.5×10^5 to 7.9×10^5 M^{-1} as shown in Table 4. The large values of the binding constants indicate a strong interaction between the P4VP and the PVPh blocks in agreement with earlier work.[21] The binding constants are relatively concentration-independent, consistent with simple 1:1 complex formation.

Surprisingly, the binding constants do not appear to depend on the molecular weight of the PVPh blocks. Thus, the binding constant of the **16** + **8** system is slightly higher than the other two although the PVPh chain length is shorter. The occurrence of multiple binding of the relatively short P4VP block copolymers to the longer PVPh blocks would be expected to increase the binding constants. This may be due to insolubility of the higher MW PVPh-*b*-PS and PS-*b*-PVPh-*b*-PS block copolymers under the experimental conditions during which some insoluble PVPh−PS block copolymers was filtered off prior to the UV/vis measurements. Thus, the concentration of PS-*b*-PVPh block copolymers may have been overestimated.

However, other factors may have played a role. This includes the relative partitioning of methylene chloride in the polymer domains of PS-*b*-PVPh or the block copolymer complexes. For instance, the solubility of P4VP−PNLO block copolymer **6** in toluene (1 vol % CH_2Cl_2) was found to be 4.33×10^{-7} M about 4 times higher than the P4VP−PNLO block copolymer with the longer P4VP block, and the solubility of these block copolymers was highly dependent on methylene chloride concentration. Upon addition of large amounts of some of the PS-*b*-PVPh copolymers, the solubility of P4VP-*b*-PNLO in toluene/methylene chloride was decreased. For instance, addition of the PS-*b*-PVPh-*b*-PS triblock copolymer to the solution of P4VP−PNLO (**6**) the UV absorption dropped *below* the absorption in the absence of the PS-*b*-PVPh-*b*-PS copolymer. This was accompanied by the precipitation of a colored complex, indicating the formation of an insoluble P4VP-*b*-PNLO complex that would have decreased the solution concentration of the PNLO block copolymer.

The PHEMA-*b*-PMMA block copolymer showed an approximately 100 times lower binding constant than the P4VP-*b*-PNLO block copolymers using the same UV/vis methodology (K is about 4.4×10^3 M^{-1}) (Table 4). One plausible reason for this difference is the approximately 6 orders of magnitude lower acidity of the hydroxyethyl group compared to that the of phenol group, which is a better hydrogen bonding donor.[27] Another possible reason is the relatively short length of the PHEMA chain ($M_n = 700$) compared to the chain length of PVPh ($M_n = 3000-30\,000$).

Table 5. Binding Constants of PVPh-*b*-PS or to P4VP-*b*-PNLO (9) in Ethyl Acetate by UV/Vis Spectroscopy

PVPh-*b*-PS sample no.	concentrations ($\times10^6$ M) PVPh-*b*-PS	VPh or HEMA groups	K ($\times10^{-5}$ M^{-1})
16	11.8	196	1.0
	22.9	382	0.67
17	6.0	255	1.10
	10.6	451	1.80
18	1.7	214	9.2
	0.8	97	20
11	92.7	285	0.11
	41.5	128	0.20

Table 6. Binding Constants of P2(4)VP-*b*-PDMs with PVPh Determined by Viscometry[a]

polymer	M_w P2(4)VP/PDMS	M_w PVPh	$K \times 10^{-6}$ M^{-1}
P2VP-*b*-PDMS + PVPh	2300/170 000	5600	8.8
P2VP-*b*-PDMS + PVPh	900/170 000	5600	<0.5
P4VP-*b*-PDMS + PVPh	1000/167 000	2400	13.5

[a] See ref 21.

On the basis of the above, the use of a single solvent would simplify the binding studies. Table 5 summarizes the binding constants in ethyl acetate in which P4VP-*b*-PNLO (1000−11 000) has a solubility of 3.05×10^{-7} M. In this case higher apparent binding constants were obtained for the PS-*b*-PVPh-*b*-PS block copolymer in which the PVPh block is much longer than for the other two PS−PVPh block copolymers. The higher binding constants are consistent with multiple binding of the P4VP-*b*-PNLO to the longer PVPh block.

Again, the PHEMA-*b*-PMMA block copolymer which has a relatively short and weaker H-bonding PHEMA block shows a lower binding constant (order of about 10^4 M^{-1}) than the PS−PVPh block copolymers (binding constants between 10^5 and 10^6 M^{-1}), in agreement with the data obtained in toluene/methylene chloride. Unfortunately, we were not able to find solvents in which competitive H-bonding to solvent is not a factor. In this case even higher binding constants would be anticipated.

It is of interest to compare the data in Tables 4 and 5 with that obtained by Lee et al. on similar systems using viscometric methods.[21] Table 6 shows apparent binding constants obtained by a viscometric method between diblock block copolymers of 2- or 4-vinylpyridine and poly(dimethylsiloxane) in THF with a PVPh homopolymer having a MW of about 40 000.[21] The binding constants are roughly of the same magnitude as those reported in Tables 4 and 5 although this is not required, as the solvent is different. These results in Table 6 also show that the P4VP block is a much better choice as hydrogen-bond acceptor compared with P2VP as the latter appears to bind much less strongly (factor of at least 10) to the PVPh donor block. Thus, the nitrogen atom on P4VP is a better proton acceptor than P2VP presumably because of steric factors.

Experimental Section

Materials. High-vacuum and break-seal techniques were used in all anionic polymerizations carried out in THF using reported methods.[28] Monomers, capping reagents, and block copolymers were synthesized according to the procedures we reported earlier.[14,29] All monomers and capping reagents were distilled under vacuum over CaH_2. Styrene and 4-vinylpyridine were further distilled over potassium mirrors. Diphenylethylene (DPE) was reacted with *t*-BuLi until a red color was observed and then vacuum distilled and sealed into ampules. Monomers were diluted with THF in a vacuum and stored at −10 °C before use. DMF and CH_2Cl_2 were distilled over CaH_2.

4-(*tert*-Butyldimethylsilyloxy)styrene (BDMSS). Vinylphenol was synthesized by hydrolysis of 25 mL of *p*-acetoxystyrene by stirring with 22 g of KOH in 370 mL of methanol/H_2O (1/1,v/v) for 3 days.[30] Dry ice (30 g) was then added to the solution. The monomer was extracted with petroleum ether/ethyl acetate (4:1, v/v) and then dried over Na_2SO_4. After evaporation of the solvent the product was recrystallized twice from hexane. 4-Vinylphenol (14.1 g) was stirred with a 24.7 g of *tert*-butyldimethylsilyl chloride (TBDMS) in 100 mL of dried DMF in the presence of 25.3 g of imidazole at 0 °C for 1 h and then stirred at room temperature under argon overnight.[19] A large amount of water was used to extract DMF. From ^1H NMR it was clear that the DMF signal disappeared only after washing with 500 mL of water. After addition of chloroform (100 mL) and washing with 100 mL of 5% NaOH and a large quantity of water (water:DMF = 20:1), the chloroform layer was dried over $MgSO_4$ overnight, and the solvent was removed by distillation. The product was vacuum-distilled (80 °C/1 mmHg) and stirred with CaH_2 overnight. The TBDMSS was then vacuum-distilled over fresh CaH_2, diluted with THF, and stored in ampules at −10 °C. The ^1H NMR peaks were assigned as follows: $Si-CH_3$, 0.042 ppm (s); $C-CH_3$, 0.829 ppm (s); $-CH$, 6.621, 6.655 ppm (d); $-CH$, 7.111, 7.148 ppm (d); $=CH$, 6.441, 6.485, 6.512, 6.555 ppm (q); $=CH_2$, 4.947, 4.990, 5.415, 5.484 ppm.

4-(*tert*-Butyldimethylsiloxy)bromomethylbenzene. Cresol (5.4 g) and 8.16 g of imidazole were mixed in 30 mL of dried DMF. *tert*-Butyldimethylsilyl chloride (6.5 g) in 15 mL of DMF solution was added dropwise under argon at 0 °C. After stirring at 0 °C for 1 h, the mixture was stirred at room temperature overnight. Chloroform (30 mL) was added before washing with 500 mL of water. The chloroform layer was dried over solid $MgSO_4$. After filtration and solvent removal the product was vacuum distilled (52−55 °C/0.3 mmHg). $Si-C\mathit{H}_3$, 0.189 ppm (s); $C-C\mathit{H}_3{}^t$, 0.999 ppm (s); $C\mathit{H}_3$, 2.291 ppm(s); $C\mathit{H}$, 6.732, 6.767 ppm (d); $C\mathit{H}$, 7.017, 7.051 ppm (d).

4-*tert*-Butyldimethylsiloxytoluene (2.22 g) was then stirred with 1.6 g of recrystallized *N*-bromosuccinimide (NBS) in 10 mL of CCl_4 in the presence of 0.02 g of benzoylperoxide at reflux temperature under argon overnight. After evaporation of CCl_4 the product was vacuum distilled and then distilled from CaH_2 on the vacuum line. Proton NMR spectra: $Si-C\mathit{H}_3$, 0.050 ppm (s); $C-C\mathit{H}_3$, 0.828 ppm (s); $Br-C\mathit{H}_2$, 4.336 ppm (s); $C\mathit{H}$, 6.625, 6.659 ppm (d); $C\mathit{H}$, 7.091, 7.125 ppm (d).

End-Functionalization of P4VP. One mL of purified 4-vinylpyridine dissolved in THF was added dropwise into 1.5 $\times 10^{-3}$ mol of *t*-BuLi and DPE in 30 mL of THF at −78 °C. An excess of a THF solution of 4-*tert*-butyldimethylsiloxybromomethylbenzene was added into the living polymer solution so that the red color of the living polymer disappeared. The solution was then poured into hexane, and the precipitate was filtered. The 4-(*tert*-butyldimethylsiloxy)bromomethyl polymer derivative was treated with 3 mL of THF solution of Bu_4NF (1.0 M) at room temperature for 3 h. The phenol end-functionalized P4VP was poured into hexane, filtered, and dried in a vacuum oven overnight.

UV/vis Analysis. P4VP-*b*-PNLO copolymers **8** and **9** were dissolved at known concentrations in a small amount of methylene chloride, and toluene was then added to give toluene/methylene chloride solutions (1 vol % CH_2Cl_2). Known quantities of the PS-*b*-PVPh block copolymers were then added, and the optical densities at 456 nm were determined. The extinction coefficient of the NLO copolymers was assumed to be unaffected by the change from methylene chloride to toluene/methylene chloride. We also assumed that the absorption coefficient at 456 nm was unaffected by the formation of the block copolymer complex. This was consistent with the observation that the shape of the UV/vis spectra of the NLO block copolymers was unaffected by complex formation with PS-*b*-PVPh.

Characterization. SEC was performed on a Water HPLC system consisting of a Waters 510 HPLC pump, UK6 injector, Polymer Laboratories 500 and 10^4 Å PL gel columns, 410 RI detector, and 484 UV detector. THF containing 5% triethylamine and 10% methanol were used as elution solvent in the cases of homo- or block copolymers containing poly(4-vinylpyridine) units. A UV/vis detector tuned at the wavelength of 456 nm was used in the SEC analysis of homo- or block copolymers containing PNLO segments. Proton and ^{13}C NMR measurements were performed on a Bruker model AM-250 MHz spectrometer.

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