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Synthesis of Block Copolymers Containing a Main Chain Polymeric NLO Segment

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ABSTRACT: A novel poly-4-vinylpyridine-*b*-PNLO (nonlinear optical material)-*b*-polystyrene-*b*-poly(4-vinylphenol) tetrablock copolymer (P4VP-*b*-PNLO-*b*-PS-*b*-PVPh) was synthesized containing an NLO polymeric segment prepared by step polymerization. The tetrablock copolymer is designed to form an asymmetric lamellar structure by self-assembly prompted by the interactions between the donor and acceptor blocks which are expected to help to align the dipole moments of PNLO block into one direction. The synthesis was carried out by reaction of a P4VP-*b*-PNLO−Ph−NH_2 block copolymer containing an aniline end group with a poly(4-*tert*-butyldimethylsiloxy)styrene-*b*-PS−CO_2H (PBDMSS-*b*-PS−COOH) diblock copolymer containing a *tert*-butyldimethylsilyl-protected polyvinylphenol endowed with a carboxylic end group in the presence of diphenylphosphoryl azide (DPPA) in *N*,*N*-dimethylacetamide. After the formation of the P4VP-*b*-PNLO−PhNH−CO−PS-*b*-PBDMSS tetrablock copolymer the PVPh block was obtained by deprotection of *tert*-butyldimethylsilyl group of the PBDMSS block with tetrabutylammonium fluoride in THF. The PBDMSS-*b*-PS−COOH precursor was synthesized by initiation of 4-(*tert*-butyldimethylsilyl)oxystyrene by *tert*-butyllithium in THF at −78 °C followed by the addition of styrene and end functionalized with dried carbon dioxide gas. The end-functionalized P4VP-*b*-PNLO−Ph−NH_2 block copolymer was synthesized by step polymerization of 4-(4-(4-fluorophenylsulfonyl)phenyl)sulfonyl-4′-*N*-ethyl-N-2-(4-hydroxyphenolic)ethylazobenzene and coupling to P4VP−Ph−OH that was end-functionalized with a phenolic end group followed by end capping with 4-(4-(4-fluorophenylsulfonyl)-phenyl)sulfonyl-4′-*N*-ethyl-N-2-(4-aminophenolic)ethylazobenzene. The end-functionalized P4VP−Ph−OH was synthesized by the 1,1-diphenyl-3,3-dimethylbutyllithium-initiated polymerization of 4-vinylpyridine in THF at −78 °C followed by addition of 4-(*tert*-butyldimethylsiloxy)bromomethylbenzene.

Introduction

Nonlinear optical (NLO) materials show changes in their optical properties when light traverses such a material. Such properties can be used to store, read, or write information optically and such materials at least in principle can be used to acquire, store, transmit and process information.[1] Materials of this kind are typically made by electrostatic orientation ("poling") of the electric dipoles of chromophores or chromophore containing polymers, usually at high temperature, followed by cooling, or cross-linking in the case of polymers, to prevent subsequent chromophore disordering.

Block copolymers are capable of forming ordered microdomains[2−4] that are thermodynamically stable and such ordering may be used to complement or enhance poling-induced dipole orientation of chromophores or possibly to avoid such poling altogether. Although it is known that the morphologies of multi (more than two) block copolymers are much more complicated than the simple diblock copolymers, block-copolymers of the ABC type can form a variety of morphologies including multilayer lamellar morphologies. [5−7]

Thus, the deposition of an ABC block copolymer containing a main chain NLO B block onto a surface (S) that interacts chemically with, say, the A block may be expected to lead to lamellar self-assembly of the block copolymer in the sequence S−$(ABC)_n$ABC.... Assuming that a B segment has directionality (nonzero dipole of the stretched chain segment) such an assembly may be expected to lead to unidirectional ordering of this segment as it spans the distance between the A and C domains.[8]

However, ABC triblock copolymers with a lamellar morphology have a strong tendency to self-assemble in the block sequence: S−ABCCBAABCCBA... etc., since this minimizes the number of lamellar interfaces (Scheme 1). Thus, the dipole moment of an NLO B block arising from a main chain group is canceled. This may not the case for an ABCD tetrablock copolymer in which A (acceptor) and D (donor) blocks are capable of strong association and C is a block incompatible with B.[9] Thus, cooperative and strong interactions between relatively short A and D block may be capable of overcoming the above self-compensating lamellar sequence and give rise to a S......ABCD......ABCD......ABCD...... alignment in which the directionality of the B block is preserved (Scheme 1). The short lengths of the A and D blocks are expected to give the tetrablock copolymer a diblock copolymer character and this would be expected to lead to lamellar morphologies if the B and C blocks are of comparable lengths.

Here we report the synthesis of ABCD tetrablock copolymers containing short poly(4-vinylpyridine) (H-bond acceptor, A) and polyvinylphenol (H-bond donor, D) blocks, a directionally asymmetric main chain B segment containing chromophores with interesting and pronounced NLO character and a polystyrene C segment that is incompatible with the B block. The B block is synthesized by step polymerization.[10] We also report the synthesis of precursors of diblock copolymers and related block copolymers capable of cooperative H-bonding.

H-bonding was chosen as the mode of interaction between the A and D blocks, as this type of interaction

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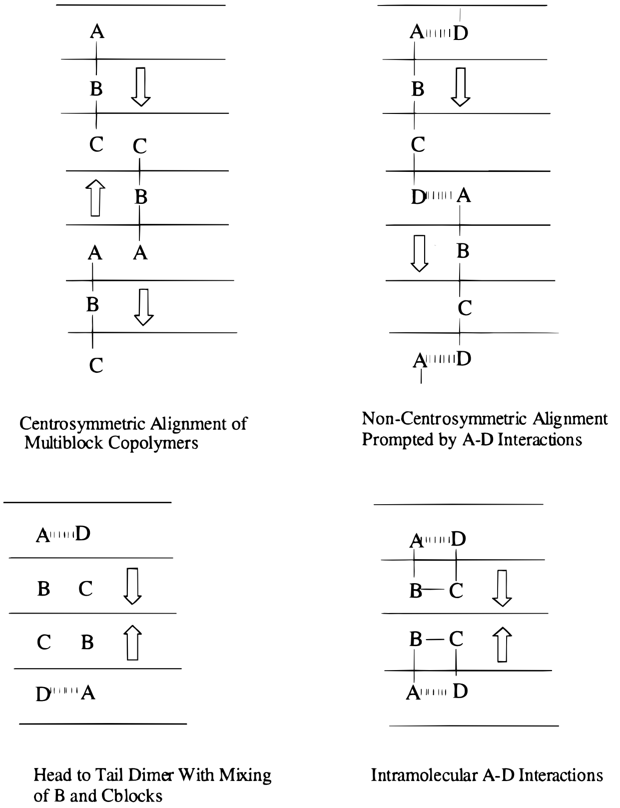
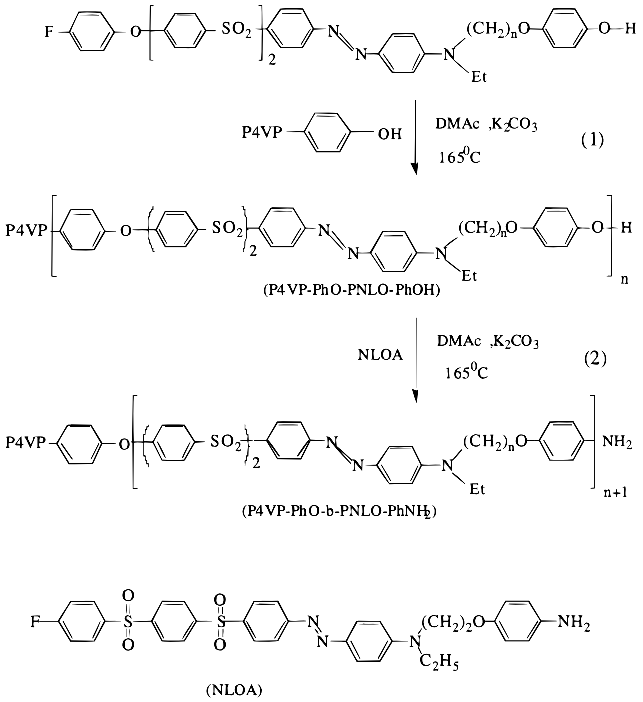
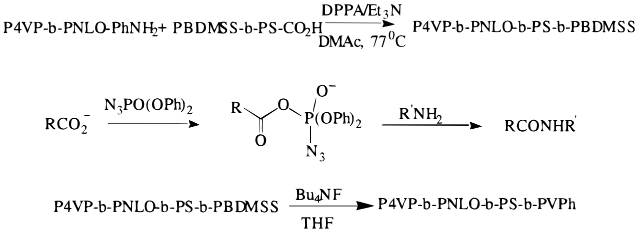
Scheme 1. Association of Tetrablock Copolymers Having a Main Chain Dipolar B Block a B-Incompatible C Block and Hydrogen Bond Acceptor (A) and Donor (D) Blocks



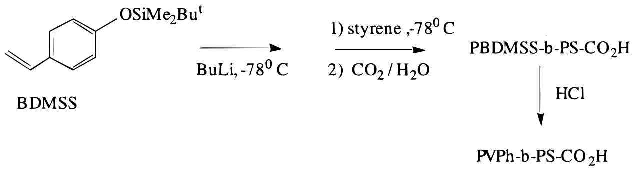
Scheme 2. Synthesis and Aniline End-Functionalization of P4VPy-*b*-PNLO



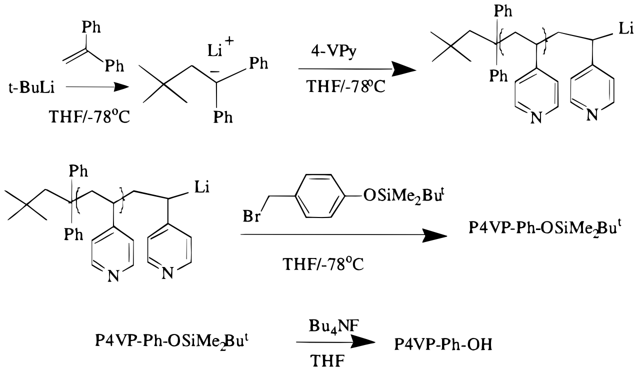
Scheme 3. Synthesis and Deprotection of the P4VP-*b*-PNLO-*b*-PS-*b*-PBDMSS



Scheme 4. Synthesis of PBDMSS-*b*-PS−CO₂H



Scheme 5. Synthesis of Phenol End-Functionalized Poly(4-vinylpyridine)



tends to give rise to strong cooperative interactions between polymer segments.[11] Examples of blocks that are H-bonding donors and subject to convenient control of block length and MW distribution are poly-2-hydroxyethyl methacrylate (PHEMA) and polyvinylphenol. Both of these polymers are accessible through anionic polymerization of the corresponding protected monomers.[12,13] Examples of narrow distribution polybases accessible through convenient anionic polymerization techniques are poly-4-vinylpyridine (P4VP) or P2VP.[14]

Poly-4-vinylphenol (PVPh) and poly-4-vinylpyridine (P4VP) are known to strongly hydrogen bond.[15] For instance this interaction has been documented by IR spectroscopy in the solid state.[15] In THF binding constants on the order of 10^4-10^6 M^{-1} have been determined depending on chain structure and length.[14] The presence of the nitrogen at the 4-position makes this group more accessible than is the case with the 2-pyridyl group. Even a short length of poly-4-vinylpyridine (DP of about 10) has been shown to give strong bonding to poly-4-vinylphenol.[14]

Results and Discussion

The synthesis of a narrow distribution multiblock copolymer incorporating an NLO block synthesized by step polymerization to our knowledge has not been reported although the synthesis has been described of copolymers incorporating backbone with pendent NLO active groups.[2,16] The synthesis of the P4VP-*b*-PNLO-*b*-PS-*b*-PVPh block copolymer is summarized in Schemes 2−5.

In the following we describe first the synthesis of the PS-*b*-PVPh (CD) and P4VP-*b*-PNLO (AB) block copolymers and the exploratory chemistry that preceded it. After several efforts to determine the optimal coupling reaction linking the AB and the CD block copolymers, we settled on the amide bond for several reasons, one

Table 1. Syntheses and Deprotection of PVPh-*b*-PS and Precursors

		$M_n{}^{b,c}$	$M_n{}^{d}$	$M_w/M_n{}^{d}$
1	PBDMSS-*b*-PS	4000	19700	1.08
1a[a]	PVPh-*b*-PS	2000	17700	1.1
2	PBDMSS-*b*-PS	10300	32100	1.09
2a[a]	PVPh-*b*-PS	5100	23100	1.07
3	PBDMSS-*b*-PS	580	2290	1.17
4	PS−COOH		7000	1.24
5	PBDMSS-*b*-PS−COOH[e]	1000	8400	1.20
6	PBDMSS-*b*-PS−COOH[e]	3000	18000	1.30

[a] **1a** and **2a** were deprotected from **1** and **2** respectively. [b] M_n of the PBDMSS block determined by ^{1}H NMR,see text. [c] M_n of PVPh block calculated from PBDMSS block. [d] M_n of block copolymers determined from SEC using polystyrene standards in THF. [e] For details see ref 18c.

being the stability of the bond and its relative ease of formation and its resistance toward hydrolysis. Another reason was the convenient synthesis and end-functionalization of the A and D−C precursor segments through sequential anionic polymerization and end-carboxylation.[17]

As shown in Scheme 3, the ABCD block copolymer is synthesized by the coupling of an amino end-functionalized P4VP-*b*-PNLO (AB) diblock copolymer with a PS-*b*-PVPh diblock copolymer end carboxylated at the PS end. This approach involved two main problems. First the formation of the A−B segment required the successful end-functionalization of the P4VP block at one end and that of the PNLO block at both ends. The PVPh-*b*-PS polymer required a quantitative end-carboxylation at the PS end as well as hydroxyl group protection prior to anionic polymerization and a final deprotection step to give the polyvinylphenol block.

The second problem involved finding the most effective chemistry for the desired high yield amide coupling reactions consistent with the nature of the functional groups present in the four blocks. Because the coupling of the CD block with the AB block would involve the reaction of the end functional groups present on relatively large AB and CD segments the actual concentrations of the reactive end groups were quite low and this restriction turned out to be especially challenging

The choice of the PNLO block shown in Scheme 2 was arrived at because of convenience of synthesis and end-functionalization (see below). Furthermore, the MW of the resulting polymer is relatively easily controlled and the polymer could be readily fractionated to give acceptable MW distributions. This approach also led to the choice of end carboxylation of the polystyrene-*b*-PVPh diblock copolymer to give the PVPh-*b*-PS−CO_2H diblock precursor.

PVPh-*b*-PS−CO_2H. This block copolymer was synthesized by the *t*-BuLi initiated sequential anionic polymerization of 4-vinyl-*t*-butyldimethylsilyloxybenzene[12,13] (BDMSS) (a 4-vinylphenol protected with the *t* -butyldimethylsilyl group) and styrene in THF at −78 °C. (Scheme 4). This was followed by end-functionalization[18] with excess carbon dioxide. Thus, BDMSS was initiated with *t*-BuLi in THF at −78 °C followed by the addition of styrene and terminated by the addition of degassed water or carbon dioxide. The deprotection was carried out by either Bu_4NF or HCl (Table 1). As expected, the color of the living PBDMSS$^-$ anion initiated by *t*-BuLi was deep red and remained the same upon addition of styrene and the color disappeared completely after addition of carbon dioxide. The IR spectrum of the PS-*b*-PBDMSS shows a peak at 1706 cm^{-1} corresponding to the carboxyl group.[19] After deprotection with fluoride ion, the BDMSS signals at 0.17 and 0.97 ppm completely disappeared from ^{1}H NMR spectrum as shown in Figure 1, parts a and b.

P4VP−Ph−OH. Next we attempted the synthesis of a phenol end-functionalized poly(4-vinylpyridine) (P4VP−Ph−OH) by the anionic polymerization of 4-vinylpyridine in THF at −78 °C and end-capping with 4-*tert*-butyldimethylsiloxy bromomethylbenzene (BDSBB) followed by deprotection of the siloxy group with tetrabutylammonium fluoride (Scheme 5). After addition of BDSBB the characteristic orange-red color of the living P4VP disappeared indicating the alkylation of the polymer anion. After the deprotection with fluoride in THF at room temperature a P4VP was obtained containing a phenolic end group (P4VP−Ph−OH) as demonstrated by integration of the proton NMR spectrum shown in Figure 2, parts a and b. Upon reaction with fluoride the peaks at 0.1 and 0.9 ppm of the P4VP precursor disappeared due to the cleavage of the TBDMS group, and there is a new peak at 4.9 ppm corresponding to the phenolic end group The extent of the functionalization was calculated as about 85 ± 10% by integrating the 2- and 6-protons of the pyridine group at 8.3 ppm (N−C*H*−) and the phenolic OH group at 4.9 ppm.

The molecular weight distributions obtained with the end-functionalized P4VP's were generally narrow (Table 2) with exception of samples **8** and **10** (MWD = 1.40) the distributions of which were broadened by a too rapid addition of monomer resulting in partial precipitation of the living polymer. As reported elsewhere this polymerization becomes heterogeneous as the MW exceeds a DP of about 40.[20,21] Nevertheless a number-average molecular weight as high as 3300 could be prepared without significant broadening.

P4VP-*b*-PNLO. The P4VP−PNLO block copolymers (Table 3, compounds **12** and **13**) were synthesized by the potassium carbonate catalyzed reaction of P4VP−PhOH (Table 2, compounds **7** and **9**) and 4-(4-(4-fluorophenylsulfonyl)phenyl)-sulfonyl-4′-*N*-ethyl-*N*-2-(4-hydroxyphenolic)ethylazobenzene (the NLO monomer) in *N*,*N*-dimethylacetamide (DMAc) at 165 °C (Scheme 2, eq 1).[10] Also two P4VP−PNLO block copolymers (Table 3, compounds **14** and **15**) endowed with an amino end group at the PNLO terminus (P4VP-*b*-PNLO−NH_2) were synthesized in a similar manner but with end capping of the P4VP-*b*-PNLO with 4-(4-(4-fluorophenylsulfonyl)phenyl)sulfonyl-4′-*N*-ethyl-*N*-2-(4-aminophenolic)-ethylazobenzene (Scheme 2, eq 2). Figure 3 shows the ^{1}H NMR of the P4VP-*b*-PNLO−Ph−NH_2 diblock copolymer **14**. The aromatic region consists of two broad bands centered at about 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-/4-pyridine protons, respectively. The $-NCH_2C\mathit{H}_2O$, $-NC\mathit{H}_2CH_2O$, and $-NC\mathit{H}_2CH_3$ protons of the NLO repeat units are clearly visible at 4.2, 3.8, and 3.6 ppm respectively together with the corresponding $-NCH_2C\mathit{H}_3$ 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. The NMR integration is consistent with the composition of the block copolymer calculated from the SEC data of the P4VP precursor and that of the block copolymer. Furthermore, upon addition of an aqueous HCl to a solution

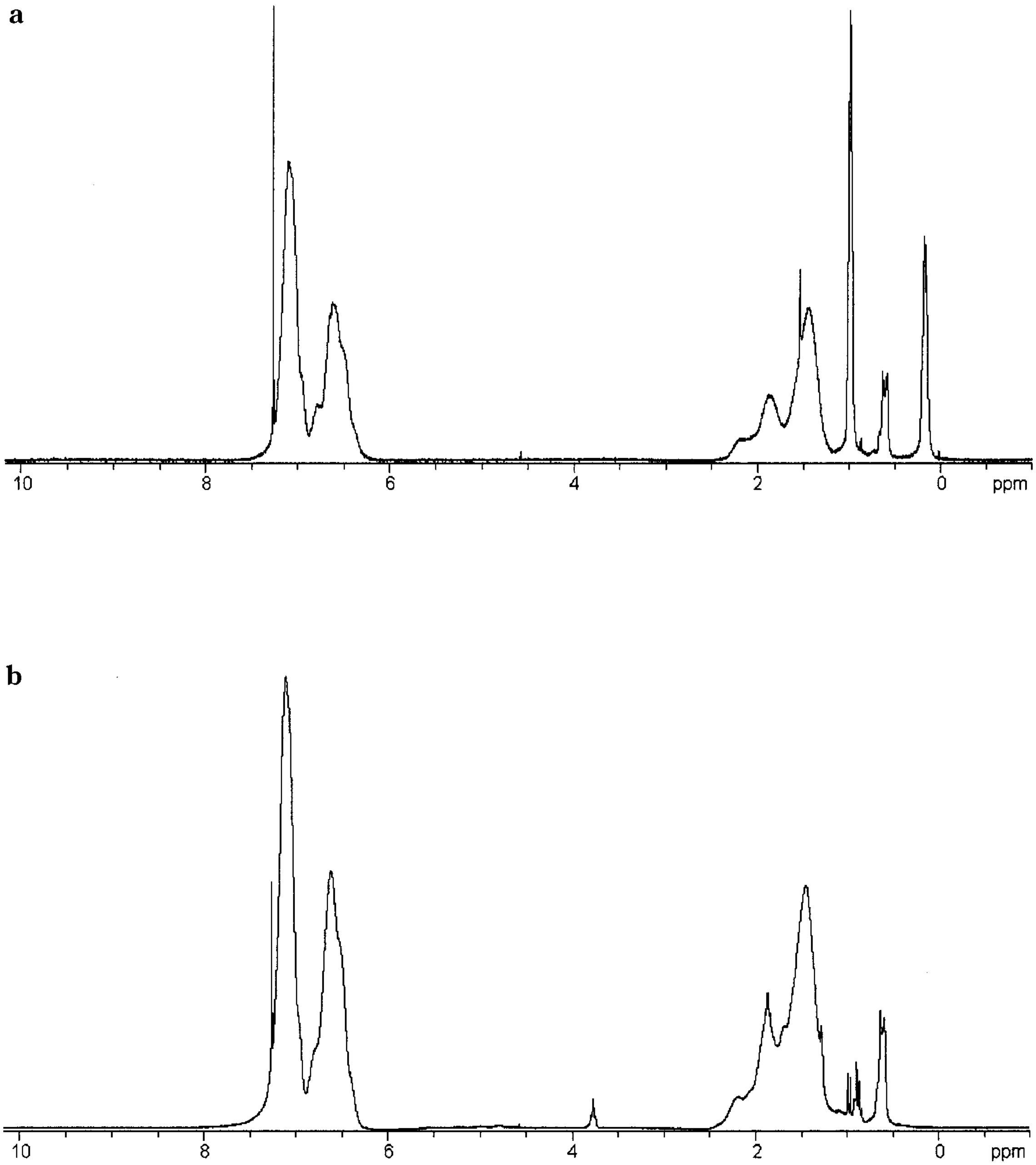


Figure 1. (a) Proton NMR (250 MHz) of PS-*b*-PBDMSS in $CDCl_3$. (b) Proton NMR (250 MHz) of PS-*b*-PVPh in $CDCl_3$.

of the P4VP-*b*-PNLO block copolymer **13** in CH_2Cl_2, the aqueous layer showed the red color 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 confirms the protonation of the P4VP block and the subsequent partitioning of the diblock copolymer into the acidic aqueous layer. However the presence of a small amount of the PNLO homopolymer in the P4VP-*b*-PNLO block copolymer cannot be ruled out.

PS-*b*-PNLO. A major concern in coupling of the AB and CD blocks shown in Scheme 2 is the low concentration of the amino and carboxyl functional groups due to the relatively large mass of the polymeric reagents. Thus, we wished to explore the scope of the reaction by studying the coupling reaction of a carboxyl end-functionalized polystyrene (Table 1, compound **4**) with an amino end-functionalized PNLO polymer as illustrated in Scheme 3.[22]

The coupling between PS−COOH and PNLO−NH_2 was first attempted by heating a 13 wt % solution of the two polymers in DMAc /toluene(70/30, V/V) under reflux (110 °C) for 96 h. The principal reason for the long reaction time was the anticipated low reaction rate due to the very low concentration of the reactive groups. Although the MW of the block copolymer was increased compared to that of the precursors, the increase in the peak MW from about 7000 of both blocks to 10 100 for the block copolymer was insufficient and consistent with some chain cleavage of the PNLO block at this temperature (Table 3, compound **16**).

P4VP-*b*-PNLO-*b*-PS. A further concern in the synthesis of the tetrablock copolymer was the amide coupling reaction in the presence of the P4VP block that might be expected to involve the deprotonation of the carboxylic end group by the basic P4VP block. This could interfere with the formation of the amide bond.[23] The synthesis of this triblock copolymer was attempted by

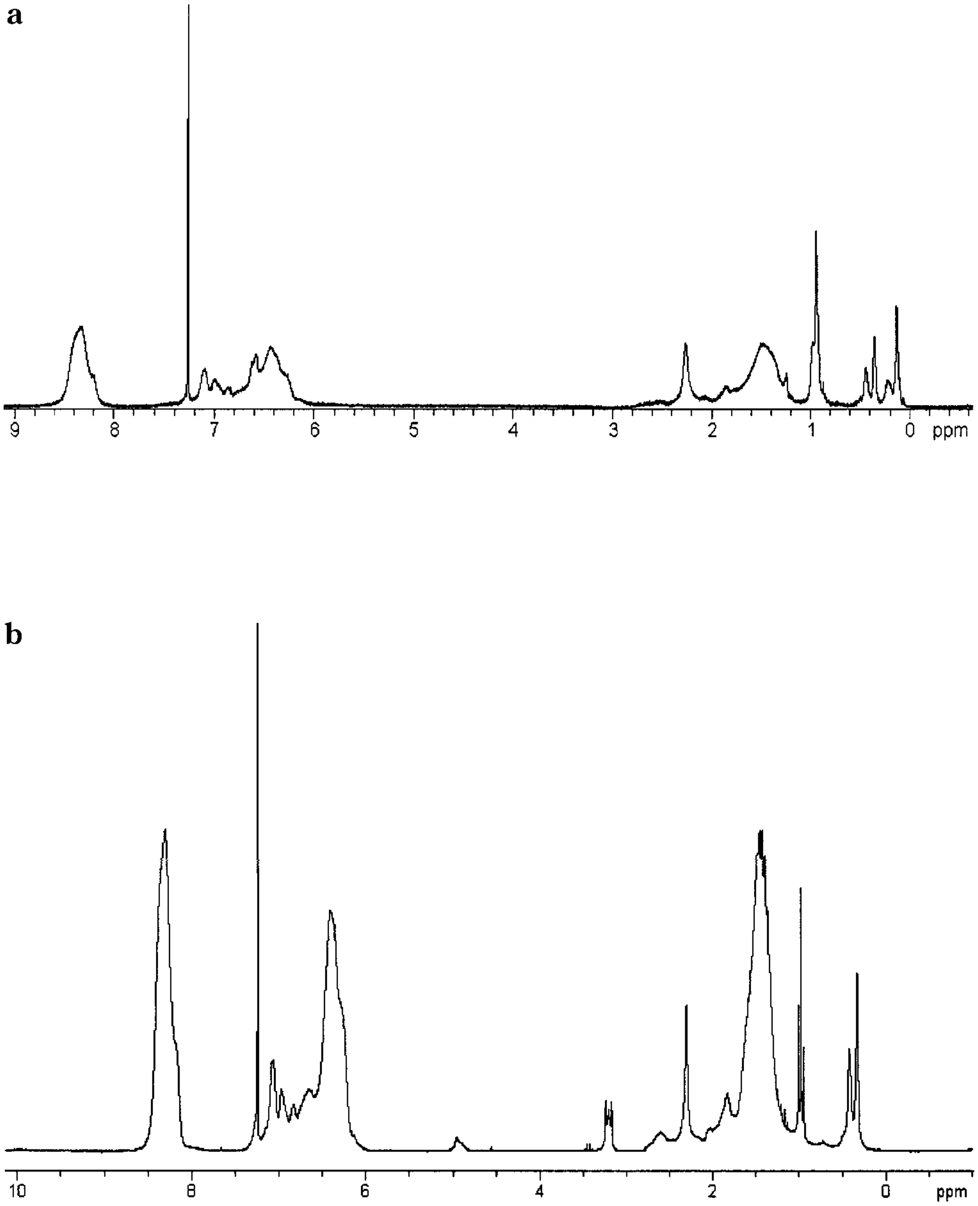


Figure 2. (a) Proton NMR (250 MHz) of P4VP−Ph−OSiBu^{t}Me$_2$ in CDCl$_3$. (b) Proton NMR (250 MHz) of P4VP−Ph−OH in CDCl$_3$.

Table 2. Synthesis and End Functionalization of Poly-4-vinylpyridine[a]

		M_p	M_n	M_w/M_n	degree of functionality[b]
7	P4VP−Ph−OH	1100	1150	1.16	85%
8	P4VP−Ph−OH	1400	1530	1.4	80%
9	P4VP−Ph−OH	4600	3300	1.25	
10	P4VP	1400	900	1.4	
11	P4VP	900	800	1.3	

[a] Molecular weights determined by SEC in THE/Et$_3$N using polystyrene standards (see text). [b] Determined by proton NMR, see text.

the reaction between P4VP-*b*-PNLO−NH$_2$ (**15**) and PS−COOH (**4**) under a variety of conditions (Table 3, compound **17**). However, heating in DMAc at 145 °C under argon did not lead to quantitative coupling as the MW increase of the block copolymer (M_n = 9100) was less than the expected value of 10 000.

This may have been due to the deprotonation of the carboxylic acid of the PS by the P4VP block. However at 145 °C and in the presence of added toluenesulfonic acid (half equivalent with respect to the P4VP unit) again a smaller than expected molecular weight increase of the polymer product was observed. At higher temperature and under otherwise similar conditions the molecular weight of the copolymer product decreased instead. Evidently under these conditions, the coupling and cleavage reactions occurred at the same time with the cleavage reactions dominating at the higher temperatures. To avoid this side reaction, we used an alternate diphenylphosphoryl azide- (DPPA-) mediated coupling reaction for the synthesis of the tetrablock copolymers (see below).

P4VP-*b*-PNLO-*b*-PS-*b*-PBDMSS. From the preceding, the above conditions appeared to lead to both coupling and decomposition of the PNLO block. Furthermore, there are other potential difficulties in the coupling of the P4VP-*b*-PNLO and the PS-*b*-PBDMSS blocks. For instance fluoride ion is generated during the synthesis of the PNLO segment and this may lead to the premature deprotection of the *tert*-butyldimethylsiloxy group of the PBDMSS block prior to coupling. Thus, the potassium fluoride generated during the formation of the PNLO segment was removed by care-

Table 3. Synthesis and Characterization of PNLO-Containing Block Copolymers

block copolymers^a		M_n of blocks^b	M_n^{e}	M_w/M_n^{e}
12	P4VP(**7**)-*b*-PNLO	1150/14650^c	15800	1.4
13	P4VP(**9**)-*b*-PNLO	3300/13700^c	17000	2.0
14	P4VP(**7**)-*b*-PNLO−Ph−NH_2	1150/9850^c (9500^d)	11000	2.0
15	P4VP(**7**)-*b*-PNLO−Ph−NH_2	1150/1850^c	3000	2.0
16	PNLO-*b*-PS(**4**)	3100/7000^c	10100	2.8
17	P4VP-*b*-PNLO(**15**)-*b*-PS(**4**)	1150/1850/7000	9100	2.0
18	P4VP-*b*-PNLO(**14**)-*b*-PS-*b*-PBDMSS(**5**)	1150/9850/7400/1000	16000	2.27
19	P4VP-*b*-PNLO(**14**)-*b*-PS-*b*-PBDMSS(**6**)	1150/9850/15000/3000	25100	1.37
20	P4VP-*b*-PNLO-*b*-PS-*b*-PVPh (**19**)	1150/9850/15000/1600	21700^f	

^{a} Numbers of precursors in Tables 1−3 in parentheses. ^{b} For molecular weights of precursor blocks, see Tables 1−3. ^{c} Molecular weights of PNLO blocks estimated from SEC MW's of block copolymers. ^{d} Determined by ^{1}H NMR. ^{e} Determined by SEC using polystyrene standards. ^{f} Calculated from the M_n of the precursor **19**.

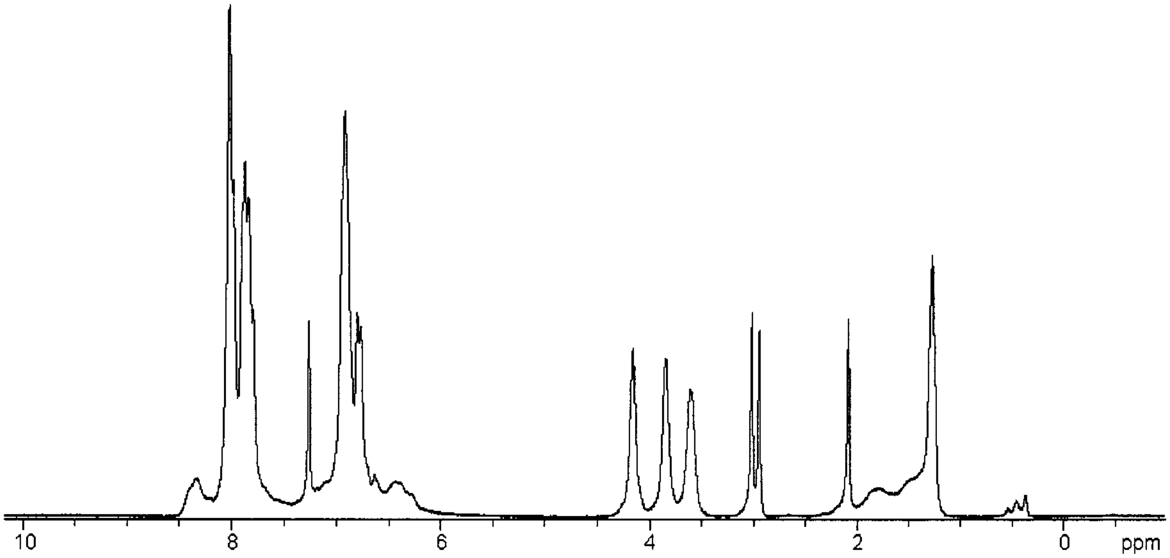


Figure 3. Proton NMR (250 MHz) of P4VP-*b*-PNLO−Ph−NH_2 in $CDCl_3$.

fully extracting the P4VP-*b*-PNLO copolymer with water.

The synthesis of the P4VP-*b*-PNLO-*b*-PS-*b*-PBDMSS tetrablock precursor was first attempted by the reaction of precursors **5** and **14** at 77 °C in DMAc overnight. In this case the molecular weight of the intended block copolymer product obtained by SEC was much less than the expected value of 19 400 (Table 3, compound **18)** This reaction at higher temperatures did not meet with success either as SEC analysis showed that the molecular weight decreased significantly compared to that of P4VP-*b*-PNLO precursor presumably due to cleavage of the PNLO block. Attempts at coupling the two diblocks in CH_2Cl_2 or CCl_4 in the presence of dicyclohexylcarbodiimide (DCC) were also unsuccessful as judged from SEC chromatograms of the reaction products.

The synthesis of the P4VP-*b*-PNLO-*b*-PS-*b*-PBDMSS tetrablock precursor was then attempted by the coupling of P4VP-*b*-PNLO−Ph−NH_2 (**14**) with PBDMSS-*b*-PS−CO_2H(**5**) using the Yamazaki reaction involving the presence of triphenyl phosphite and pyridine in the presence of LiCl at 185 °C in *N*-methylpyrrolinone (NMP).[24] However, despite the success of the Yamazaki reaction in polycondensation reactions,[25] the molecular weight of the intended P4VP-*b*-PNLO-*b*-PS-*b*-PBDMSS block copolymer did not increase with respect to that of the precursors but decreased instead at this high temperature (185 °C) consistent with thermal decomposition. This failure could also be due to the formation of a phenyl ester from the PS−COOH and the phenol generated from the phosphite.

Eventually the tetrablock copolymer was synthesized successfully at room temperature by the coupling of P4VP-*b*-PNLO−Ph−NH_2 (**14**) with PBDMSS-*b*-PS−COOH (**5** or **6**) in the presence of 1 equiv of diphenylphosphoryl azide (DPPA) and 2 equiv of triethylamine with respect to the reactive end groups (Table 3, compounds **18** and **19**) (Scheme 3).[26] The activation of the carboxyl group in the form of an acyl azide allows the coupling reaction at low temperature without incurring thermally induced chain cleavage. An advantage of the reaction is also that it is not necessary to have the carboxyl group in the acid from.[27] Unlike for the case of uncatalyzed formation of the amide linkage, the reaction allows the presence of traces of water which is the biproduct of the coupling reaction.[28]

Although ambient temperature is known to be sufficient for the formation of the amide bond in this case the rate of reaction at room temperature was expected to be insufficient due to the low concentration of the end functional groups of the polymeric blocks. At 65 °C and at a relatively low concentration (5.5×10^{-4} M) of the reactive end groups of precursors **5** and **14** the increase in the apparent SEC number-average molecular weight was close (16 000 vs 19 400) to that predicted from the MW of the diblock precursors (Table 3, compound **18**). Again, increasing the reaction temperature to 93 °C or higher caused a decrease in the molecular weight indicating cleavage of the PNLO segment.

At higher concentrations (19 wt % of precursors or 6.9×10^{-3} M of functional groups), the reaction tem-

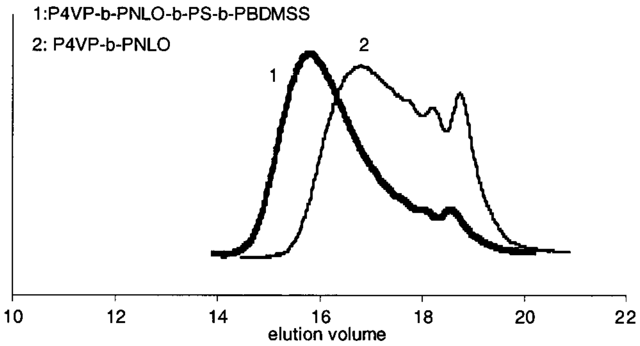


Figure 4. SEC chromatogram of P4VP-*b*-PNLO and P4VP-*b*-PNLO-*b*-PS-*b*- PBDMSS (Table 3, compound **19**).

perature could be kept at 25 °C. The coupling product was isolated as a red powder by precipitation into methanol and drying on the vacuum line. No molecular weight increase could be observed after 2 days and SEC analysis gave reasonable agreement with the expected elution volume (Figure 4, Table 3, compound **19**). It should be pointed out that the small shoulder seen in Figure 4 is due to the presence of a low MW PNLO, possibly cyclic, polymer that was generated in the course of the step polymerization and that could not be removed readily by fractional precipitation. It is not seen in cases where thermal decomposition of the PNLO block occurred.

The PNLO content of sample **19** was also analyzed by visible spectroscopy. Consistent with the reported absorption maximum the block copolymer dissolved in dry DMAc showed an absorption maximum at 473 nm that was identical to that observed for the homopolymer. Using the extinction coefficient of the PNLO precursor block copolymer (**14**) determined in methylene chloride ($6.75 \times 10^5\ \mathrm{L{\cdot}mol^{-1}{\cdot}cm^{-1}}$) the PNLO content of **19** was determined as 33.4 wt % which is almost exactly the same value as the 34.0 wt % calculated from the composition of the two block copolymers **14** and **6**.

P4VP-*b*-PNLO-*b*-PS-*b*-PVPh. The P4VP-*b*-PNLO-*b*-PS-*b*-PBDMSS tetrablock copolymer, **19**, was deprotected with tetrabutylammonium fluoride in THF at room temperature to give a solution of the P4VP-*b*-PNLO-*b*-PS-*b*-PVPh block copolymer (Scheme 5). The final block copolymer was isolated by precipitation into methanol and drying on the vacuum line. At the last stage of the deprotection procedure the polymer solution was hard to stir in THF due to gelation. This appears to be due to the intermolecular formation of a network structure by hydrogen bonding between the P4VP and PVPh blocks. However DMAc and NMP are good solvents as they are good hydrogen bond acceptors.

The NMR spectrum of the deprotected sample (Table 3, compound **20**) in deuterated DMAc is shown in Figure 5. The aromatic region consists of two broad bands centered at about 7.1 and 6.6 ppm corresponding to the aromatic protons of the PS and the PNLO blocks, in addition to a small contribution of the PVPh block (see Figures 1 and 3). The $-\mathrm{NCH_2C}H_2\mathrm{O}$ and $-\mathrm{NC}H_2\mathrm{CH_2O}$ protons of the NLO repeat units are clearly visible at 4.27 and 3.95 ppm, respectively, together with the corresponding $\mathrm{NCH_2C}H_3$ methyl group at 0.97 ppm. The methylene and methine protons are visible between 1.5 and 2 ppm. The 2(6)- and 3(5)-pyridine protons of the P4VP block seem to appear at about 8.3 and 7.9 ppm, respectively. The apparent large downfield shift of the 3(5)-proton is surprising but may be caused by the formation of the phenol-pyridine H-bond that is expected to shift these protons downfield. The increased resolution of both of the pyridine protons is curious and unexplained. The OH proton of the small PVPh block is not visible and may be obscured by the large water absorption at 3.6 ppm or may be broadened beyond recognition as a result of H-bonding.

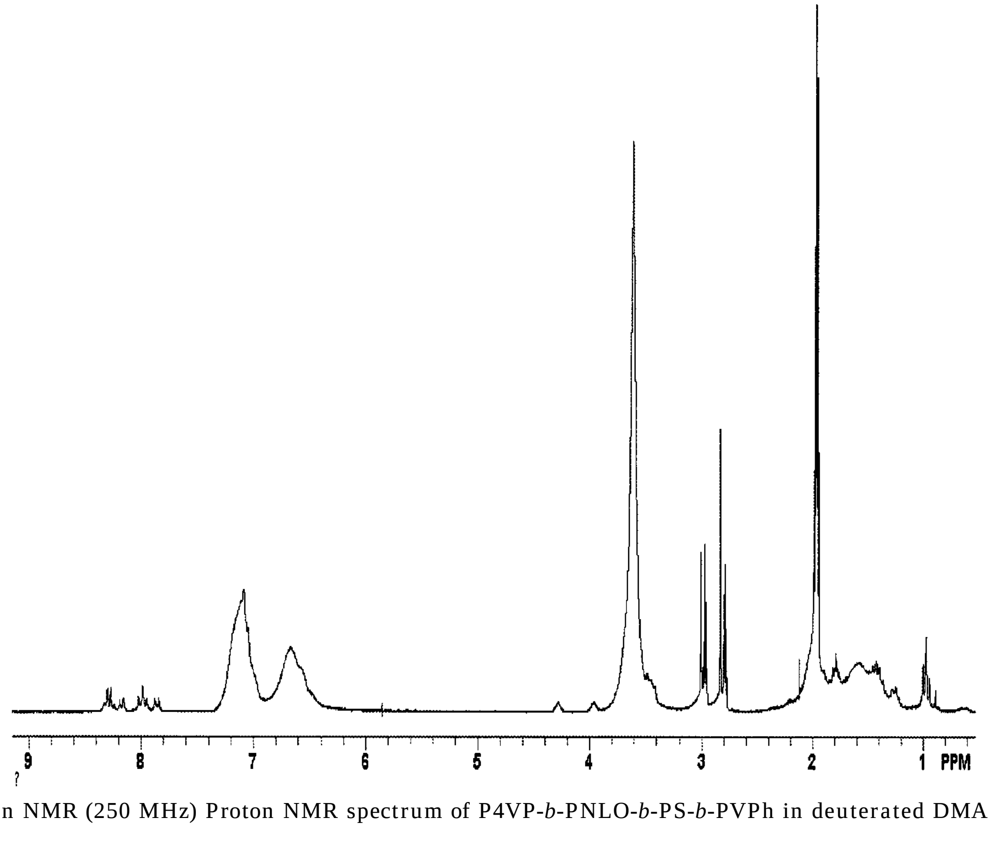


Figure 5. Proton NMR (250 MHz) Proton NMR spectrum of P4VP-*b*-PNLO-*b*-PS-*b*-PVPh in deuterated DMAc.

The nature of the block copolymer was also confirmed by electron microscopy carried out on unstained block copolymer **20**. The electron micrograph shows well-defined cylindrical PNLO domains with widths of 20−50 nm in what appears to be an otherwise unstructured single phase.[29]

Thermal gravimetric analysis of the AB and CD block copolymers showed that the P4VP-*b*-PNLO copolymer starts to degrade at 250 °C, while PS begins to degrade at 300 °C. The PVPh appears to be stable until 350 °C.[30,31] This is also shown in a TGA of the tetrablock copolymer confirming that the P4VP-*b*-PNLO-*b*-PS-*b*-PVPh copolymer is thermally stable below 250 °C.

Experimental Section

Materials. DMF and CH_2Cl_2 (Aldrich) were distilled over CaH_2. Pyridine (J. T. Baker, 99.5%) and triphenyl phosphite (Aldrich, 97%) were dried over molecular sieves; 1-methyl-2-pyrrolidone (NMP, 99.5%) and *N*,*N*-dimethylacetamide (DMAc) (Aldrich) were used without further purification. LiCl was dried by heating at 110 °C overnight on the vacuum line. Triethylamine was distilled over $MgSO_4$.

All monomers and capping reagents were distilled over CaH_2 under vacuum prior to use. Styrene and 4-vinylpyridine were also vacuum distilled from potassium mirrors and were diluted with THF before being stored at −10 °C. 1,1-Diphenylethylene (DPE) was reacted with *t*-BuLi until a red color was observed and then vacuum distilled into an ampule and diluted with THF. THF kept over Na−K alloy on the vacuum line was used as the anionic polymerization solvent.

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 to the stirred solution under argon at 0 °C. After addition, stirring was continued at 0 °C for 1 h and 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, the solvent was distilled out, and the 4-(*tert*-butyldimethylsiloxy)toluene product (BDST) was vacuum distilled (52−55 °C/0.3 mmHg). Si−CH_3: 0.189 ppm (s). C−CH_3^t: 0.999 ppm (s). CH_3: 2.291 ppm(s). C*H*: 6.732, 6.767 ppm (d). C*H*: 7.017, 7.051 ppm (d).

According to a modified procedure[32,33] BDST (2.22 g) was then stirred with 1.6 g of *N*-bromosuccinimide (NBS) in 10 mL of CCl_4 in the presence of 0.02 g of BPO at reflux temperature under argon overnight. CCl_4 was distilled off and the residue was vacuum distilled. The 4-(*tert*-butyldimethylsiloxy)bromomethylbenzene (BDBMB) product was then stirred over CaH_2 overnight, distilled on the vacuum line and stored in THF at −10 °C. Proton NMR: Si−CH_3, 0.050 ppm (s); C−CH_3, 0.828 ppm (s); Br−CH_2, 4.336 ppm (s); C*H*, 6.625, 6.659 ppm (d); C*H*, 7.091, 7.125 ppm (d).

4-(*tert*-Butyldimethylsilyl)oxystyrene (BDMSS). The synthesis and purification of this monomer is documented in the literature.[34,13] We chose to purify the monomer with CaH_2 instead of benzylmagnesium chloride. Since phenol has a pH value of 10, CaH_2 is basic enough to deprotonate the phenolic group. The other change in the preparation is the addition chloroform before the aqueous wash to remove DMF. A large amount of water was used to extract DMF. The ^{1}H NMR DMF signal disappeared only after repeated washings with 500 mL of water. 4-Vinylphenol (4VPh) 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.[34] Thirty grams of dry ice was added to the solution and petroleum ether/ethyl acetate (4:1, V/V) was used to extract the 4VPh. The extract was then dried over Na_2SO_4. After evaporation, the product was recrystallized twice from hexane. The 4VPh (14.1 g) was stirred with 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. Chloroform (125 mL) was added and washed with 100 mL of 5% NaOH solution and 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 BDMSS product was vacuum distilled over CaH_2, diluted with THF and stored in ampules at −10 °C. The proton NMR was assigned as follows: Si−CH_3, 0.042 ppm(s); C−CH_3, 0.829 ppm (s); −C*H*, 6.621, 6.655 ppm (d); −C*H*, 7.111, 7.148 ppmn (d); ═C*H*, 6.441, 6.485, 6.512, 6.555 ppm (q); ═CH_2, 4.947, 4.990, 5.415, 5.484 ppm.

Polymerizations. High vacuum and break seal techniques were used in all anionic polymerizations using reported methods.[35] Polymerizations were terminated with degassed water, methanol, or carbon dioxide.

P4VP−Ph−OH (7,8). One milliliter of 4-vinylpyridine in 5 mL of THF was added dropwise into 1.5×10^{-3} mol of DMPBL initiator in 30 mL of THF at −78 °C. A slight excess of a solution of BDBMB dissolved in THF was added into the living polymer solution until the red color of the living polymer disappeared. The polymer solutions were poured into hexane and 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. Both polymers were poured into hexane, filtered and dried in a vacuum oven.

PS−CO_2H (4) and PBDMSS-*b*-PS−CO_2H (5,6). Styrene (1.5 g) was added into 1.6×10^{-4} mol of *t*-BuLi in 30 mL of THF at −78 °C, and dried CO_2 gas was introduced into the solution until the red color of the PSLi disappeared.[18] The polymer solution was decanted into methanol and filtered. The polymer was dissolved in 20 mL of CH_2Cl_2, washed with 10 mL of aqueous HCl and distilled water, and then precipitated in 200 mL of methanol. For the IR spectrum a 5−10 wt % polymer solution in CH_2Cl_2 was dripped onto a NaCl crystal and dried. The same work up procedure was used for the analysis of the PBDMSS-*b*-PS−CO_2H diblock copolymer the only difference being the washing of the diblock copolymer in dichloromethane with dilute HCl (pH = 3−4) to avoid the deprotection of the PBDMSS block.

PS-*b*-PNLO (16). The PNLO precursor was synthesized as reported elsewhere.[10] Ten milligrams of PNLO−Ph−NH_2 having an amino end group and 10 mg of PS−CO_2H were mixed together in 1 mL of *N*,*N*-dimethylacetamide with 0.3 mL of toluene, heated to reflux under argon for 4 days using a Dean−Stark apparatus. The sample was analyzed by SEC using a UV detector.

P4VP-*b*-PNLO-*b*-PS. (17). P4VP-*b*-PNLO and PS precursors were purified by precipitation into methanol and dried. Ten milligrams of P4VP-*b*-PNLO−Ph−NH_2 (**15**) and 10 mg of PS−COOH (**4**) were mixed together in 1 mL of *N*,*N*-dimethylacetamide with 0.3 mL of toluene and a half equivalent of toluenesulfonic acid with respect to the pyridine units and heated to 145 °C using a Dean−Stark apparatus under argon overnight. A sample was withdrawn for SEC analysis. The rest was heated at reflux overnight. The product was precipitated into methanol, filtered, and dried.

PS-*b*-PNLO (16). The PNLO precursor was synthesized as reported elsewhere.[10] The precursor polymers PS−COOH and PNLO−Ph−NH_2 were purified by precipitation into methanol and dried. Ten milligrams of PNLO−Ph−NH_2 having an amino end group and 10 mg of PS−CO_2H were mixed together in 1 mL of DMAc with 0.3 mL of toluene and heated to reflux under argon for 4 days using a Dean−Stark apparatus. The sample was analyzed by SEC using a UV detector.

P4VP-*b*-PNLO-*b*-PS-*b*-PBDMSS (17). The P4VP-*b*-PNLO and PS-*b*-PBDMSS precursors were purified by precipitation into methanol and dried.

Procedure 1. Ten milligrams of P4VP-*b*-PNLO (**14**) and 10 mg of PS-*b*-PBDMSS (**5**) in 1 mL of *N*,*N*-dimethylacetamide/toluene(3/1, V/V) was heated to reflux without the presence of a catalyst under argon in a Dean−Stark apparatus. In this case and in all other cases reactions were monitored by SEC analysis.

Procedure 2. Ten milligrams of P4VP-*b*-PNLO (**14**) and 10 mg of PS-*b*-PBDMSS (**5**) were stirred with 1 equiv of DCC in CH_2Cl_2 or in CCl_4 under argon at room temperature or under reflux respectively overnight.

Procedure 3. One hundred milligrams of P4VP-*b*-PNLO (**14**) and 100 mg of PS-*b*-PBDMSS (**6**) were mixed in 3 mL of *N*-methyl-2-pyrrolidone (NMP). One milliliter of pyridine, 10 mg of triphenyl phosphite, and 0.2 g of LiCl were added and the mixture was heated at 110 °C under argon with stirring overnight.

Procedure 4. Ten milligrams of P4VP-*b*-PNLO (**14**) and 10 mg of PS-*b*-PBDMSS (**5**) with one drop of DPPA and two drops of triethylamine were stirred under argon at room-temperature overnight, or heated at 65 °C for 12 h, or heated at 93 °C for 10 h, or heated at 110 °C overnight.

Procedure-5. A 0.60 g sample of P4VP-*b*-PNLO (**14**) and 1.0 g of PS-*b*-PBDMSS (**6**) were stirred with two drops of DPPA and four drops of triethylamine in 8 mL of DMAc under argon at room temperature for 6 days. From the SEC analysis the coupling reaction did not proceed further after 2 days. The product obtained in quantitative yield was precipitated into methanol, filtered, and dried.

P4VP-*b*-PNLO-*b*-PS-*b*-PVPh. About 1 g (1.02 g) of P4VP-*b*-PNLO-*b*-PS-*b*-PBDMSS (**19**) was dissolved in 6.0 mL of a THF solution of tetrabutylammonium fluoride (1.0 M) under argon at room temperature for 4 h. The product was precipitated into methanol, filtered, and dried. The yield was almost quantitative (>95%). The copolymer is soluble in dry *N*,*N*-dimethylacetamide or NMP at ambient temperatures. However it could not be analyzed readily by SEC since it is not soluble in THF or other accessible SEC solvents. There is enough solubility in methylene chloride to allow UV/visible analysis.

Characterization. SEC was performed on a Water HPLC system consisting of: a Waters 510 HPLC pump, UK6 injector, Polymer Laboratories 500 and 10^4Å PLgel columns, 410 RI detector, and 484 UV detector. Then 5% triethylamine and 10% methanol were added to HPLC grade THF as SEC elution solvent in the cases of homocopolymers or block copolymers containing poly-4-vinylpyridine blocks. The UV/visible detector was used in the SEC analysis of homo- or block copolymers containing PNLO segments at the wavelength maximum of 456 nm. Proton and ^{13}C NMR measurements were performed on a Bruker model AM-250 MHz FT-NMR. NMR, SEC, UV/vis, and FT-IR (Perkin-Elmer spectrometer, Spectrum 2000) were used to characterize the monomers, capping reagents, and polymers.

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