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Block Copolymers of *p-tert*-Butoxystyrene with Isobutyl Vinyl Ether or Styrene Derivatives via Sequential Living Cationic Polymerization: Synthesis of Amphiphilic Macromolecules with a Poly(*p*-vinylphenol) Segment

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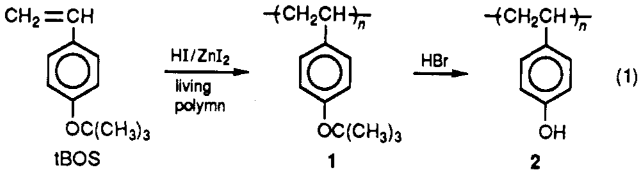
ABSTRACT: Block copolymers of *p-tert*-butoxystyrene (tBOS) with isobutyl vinyl ether (IBVE), *p*-methoxystyrene (pMOS), and *p*-methylstyrene (pMS) were synthesized by sequential living cationic polymerizations with the hydrogen iodide/zinc halide (HI/ZnX$_2$; X = I, Cl) initiating systems in toluene at −15 °C. tBOS–IBVE and tBOS–pMS block copolymers were obtained only by initiating sequential polymerization from a more reactive monomer (IBVE for tBOS; tBOS for pMS), followed by further addition of ZnX$_2$ in order to accelerate the subsequent polymerization of the second monomer from the resultant living polymer. In contrast, the tBOS–pMOS block copolymerization could be started from either of the monomers, because of their similar reactivities. These tBOS-based AB block copolymers possessed controlled molecular weights and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.04–1.22), being free from homopolymers. The poly(tBOS) segments in the block copolymers could be converted into poly(*p*-vinylphenol) segments by acidolysis with hydrobromic acid. The deprotected block polymers were insoluble in benzene and dichloromethane, which are good solvents for the starting block copolymers of tBOS.

Introduction

p-tert-Butoxystyrene (tBOS)[1–4] is a styrene derivative with a functional para substituent and is structurally similar to *p*-methoxystyrene (pMOS). Because of the electron-donating *p*-alkoxyl groups, these styrenic monomers are expected to be suited for living cationic polymerization, where the stabilization of the growing carbocation is mandatory.[5] In fact, we have recently achieved living cationic polymerizations of tBOS[4] and pMOS[6] with the hydrogen iodide/zinc iodide (HI/ZnI$_2$) initiating system.[7] Poly(tBOS) (**1**) can readily be converted into poly(*p*-vinylphenol) (**2**)[1–4,8] by treatment with hydrobromic acid (eq 1),[1b,4] and upon this deprotection, the initially hydrophobic polymer is rendered hydrophilic and soluble in methanol and aqueous alkali solution.

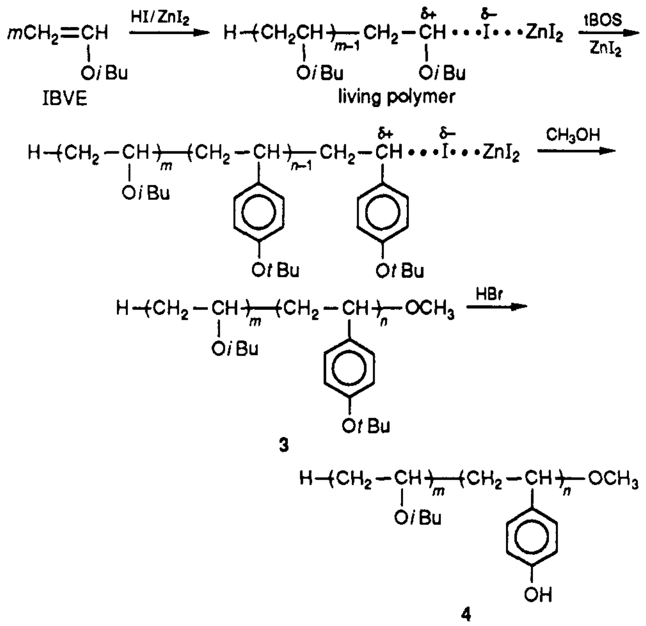


(1)

In addition to the living homopolymerizations of tBOS and pMOS, we have recently shown that sequential living cationic polymerizations of pMOS and vinyl ethers by HI/ZnI$_2$ lead to well-defined AB block copolymers.[9] This finding prompted us to synthesize similar block copolymers of tBOS with pMOS, *p*-methylstyrene (pMS), and isobutyl vinyl ether (IBVE), all of which are now known to undergo living cationic homopolymerization in the presence of the HI/ZnI$_2$ or HI/ZnCl$_2$ initiating system.[6,7,10] As an illustrative example, Scheme I shows block copolymerization of tBOS and IBVE. Because IBVE, pMOS, and pMS form hydrophobic segments, these tBOS-based block copolymers (like **3**) would give amphiphilic polymers (like **4**) upon deprotection of the *tert*-butoxyl pendant substituents into hydroxyl groups.

Another focus of this study is the effect of monomer addition sequence on blocking efficiency, in relation to the reactivity difference between the component monomers. In the pMOS–IBVE block copolymerization with HI/ZnI$_2$,[9] for example, more reactive IBVE should be polymerized first in order to obtain an AB block polymer of narrow molecular weight distribution (MWD). The opposite sequence (pMOS → IBVE) results in an unacceptably fast second-stage polymerization of IBVE, and the product shows a bimodal MWD indicative of low blocking efficiency. The estimated reactivity of the four monomers employed herein decreases in the order IBVE > pMOS ≥ tBOS > pMS and, therefore, reverse sequences of monomer addition (A → B and B → A) were compared herein for particular pairs of monomers.

Scheme I
Block Copolymerization of tBOS and IBVE



Experimental Section

Materials. tBOS (Hokko Chemicals), pMS (Tokyo Kasei), and IBVE (Tokyo Kasei) were washed with 10% aqueous sodium

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hydroxide solution and then with water and dried overnight with anhydrous sodium sulfate (for tBOS and pMS) or with potassium hydroxide (for IBVE). pMOS was prepared from *p*-methoxyacetophenone by the literature method.[11] All these monomers were then doubly distilled over calcium hydride under reduced pressure (except IBVE), and the gas chromatographic purity invariably exceeded 99.8%. Anhydrous hydrogen iodide was obtained as an *n*-hexane solution as reported.[12] ZnI_2 (Aldrich, purity >99.99%) and $ZnCl_2$ (Aldrich, 1.0 M diethyl ether solution) were used without further purification.[7] Solvents (toluene, *n*-hexane, and diethyl ether) and internal standards for gas chromatography (carbon tetrachloride and tetrahydronaphthalene) were purified by the usual methods[12] and distilled twice over calcium hydride just before use.

Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes each equipped with a three-way stopcock.[6,7] The reaction was initiated by sequential addition of prechilled solutions of hydrogen iodide (in *n*-hexane, 0.50 mL) and ZnX_2 (X = I, Cl; in diethyl ether, 0.50 mL) into a monomer solution (in toluene, 4.0 mL) containing 0.20 mL of carbon tetrachloride (for IBVE) or tetrahydronaphthalene (for the styrene derivatives) as an internal standard for gas chromatography. Immediately after completion of the first-phase polymerization, a second monomer was added in bulk to the preformed living polymer solution. In the case where the polymerization of the second monomer was too slow, an additional amount of ZnX_2 (as a diethyl ether solution) was added after the addition of the second monomer (see under Results and Discussion). After complete consumption of the second monomer had been confirmed by gas chromatography, the polymerization was terminated with prechilled methanol containing a small amount of ammonia (2.0 mL). The quenched reaction mixtures were washed with 10% aqueous sodium thiosulfate solution and then with water to remove the initiator residues, evaporated to dryness below 40 °C under reduced pressure, and vacuum-dried to give the polymers.

Polymer Characterization. The MWD of the polymers was measured by size-exclusion chromatography (SEC) in chloroform at room temperature on a Jasco Trirotar-V chromatograph equipped with three polystyrene gel columns (Shodex K-802, K-803, and K-804; exclusion limits, 5×10^3, 7×10^4, and 4×10^5, respectively; 8-mm i.d. × 300 mm each) and referactive index/ultraviolet dual detectors. The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of the polymers were calculated from SEC chromatograms on the basis of a polystyrene calibration. ^1H NMR spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ at 30 °C on a Jeol FX-90Q spectrometer. Polymer samples for NMR analysis were separated from low molecular weight residues (like tetrahydronaphthalene) by preparative SEC (with a Jasco Megapak 201 polystyrene gel column; exclusion limit, 2×10^3) in chloroform.

Acidolysis of Block Copolymers. Acidolysis of the tBOS block copolymers was carried out by treatment with hydrobromic acid.[1b,4] A typical example was as follows: A sample of the block copolymer of tBOS and IBVE (0.20 g; tBOS/IBVE = 1/1 molar ratio; Table I, entry 1) was dissolved in 1,4-dioxane (20 mL), and 8.6 N hydrobromic acid (0.42 mL; Wako Chemicals; 5 equiv to the *tert*-butoxyl units in the polymer) was added. The solution was magnetically stirred at room temperature for 24 h and poured into water (200 mL). The precipitated polymer was filtered off, washed several times with deionized water, and freeze-dried twice from 1,4-dioxane to give a *p*-vinylphenyl–IBVE block copolymer in near quantitative yield (0.16 g); see the text for characterization.

Results and Discussion

Block Copolymerization of tBOS and IBVE. On the basis of the results for pMOS–IBVE block copolymerization previously reported (see also Introduction),[9] the tBOS–IBVE counterpart was first examined by starting from IBVE. Thus, IBVE was polymerized in toluene at −15 °C with the HI/ZnI_2 (10/0.20 mM) initiating system,[7] and when the IBVE feed was depleted completely, tBOS was added in bulk into the reaction mixture. The poly(IBVE) obtained under these conditions was living;[7] the MWD was very narrow ($\bar{M}_w/\bar{M}_n < 1.1$); and the $\bar{M}_n$ was in good agreement with the calculated value assuming that one polymer chain is formed per molecule of hydrogen iodide (Figure 1A). However, the added tBOS was hardly polymerized, because the ZnI_2 concentration was too low for tBOS, which is much less reactive than IBVE in cationic polymerization.[4]

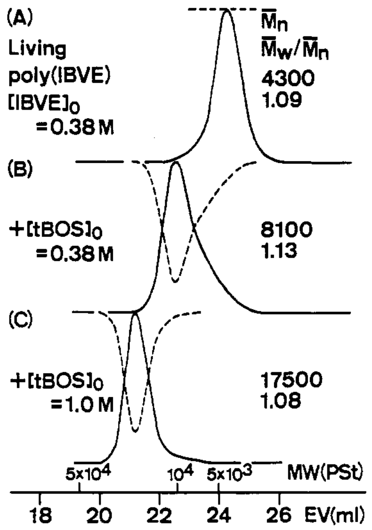


Figure 1. Polymer MWDs in the IBVE–tBOS block polymerization in toluene at −15 °C: (A) living poly(IBVE); (B and C) block polymers from prepolymer A. $[HI]_0$ = 10 mM, $[ZnI_2]_0$ = 0.20 mM (+5.0 mM for the second stage in B and C); conversions are ca. 100% for both monomers. See the following table for other reaction conditions. (—) RI; (- - -) UV at 254 nm.

	first stage		second stage	
sample	monomer (M)	time	monomer (M)	time
A	IBVE (0.38)	14 min		
B	IBVE (0.38)	14 min	tBOS (0.38)	48 h
C	IBVE (0.38)	14 min	tBOS (1.0)	48 h

Treatment of this quiescent solution with an additional amount of ZnI_2 (5.0 mM), on the other hand, led to quantitative polymerization of the added tBOS feed. Parts A and B of Figure 1 show the MWDs of two samples that were obtained in this way by addition of 0.38 and 1.0 M of tBOS, respectively, into the solution of the preformed living poly(IBVE) (shown in Figure 1A). The polymers exhibited narrow MWDs without tailings. The MWD curves were also featured by strong ultraviolet absorptions at 254 nm, where the starting poly(IBVE) is transparent (Figure 1A) but poly(tBOS) strongly absorbs. The ultraviolet and refractive index MWD traces were almost identical, indicating the incorporation of tBOS units over the entire molecular weight range. The ^1H NMR spectra of the block copolymers (see below) were fully consistent with the expected AB block structure and showed that the tBOS/IBVE compositions (based on the integrated peak intensity ratios) are in good agreement with the feed molar ratios of the two monomers (Table I, entries 1 and 2). Thus, AB block copolymers of IBVE and tBOS were synthesized with nearly perfect blocking efficiency.

The reverse order of monomer addition (i.e., from tBOS to IBVE) were also examined for the tBOS–IBVE block copolymerization (Figure 2A–C). Living poly(tBOS) was prepared in toluene at −15 °C with the HI/ZnI_2 system (10/5.0 mM; Figure 2A; $\bar{M}_w/\bar{M}_n < 1.1$; one chain per hydrogen iodide molecule),[4] and IBVE was subsequently added at two concetrations. Note that the ZnI_2 concentration for the first-stage polymerization was 25 times higher than in the block copolymerization where IBVE was polymerized first (Figure 1A).

Table I
Block Copolymers of *p-tert*-Butoxystyrene via Sequential Living Cationic Polymerization by HI/ZnI$_2$[a]

no.	block polymer (A/B)[b]	$\bar{P}_A/\bar{P}_B$[c] calcd[d]	$\bar{P}_A/\bar{P}_B$[c] obsd[e]	$\bar{M}_n$[f]	$\bar{M}_w/\bar{M}_n$[f]	sample
1	IBVE/tBOS	38/38	38/37	8 100	1.13	Figure 1B
2	IBVE/tBOS	38/100	38/94	17 500	1.08	Figure 1C
3	tBOS/pMOS	38/38	38/40	12 100	1.05	Figure 3B
4	tBOS/pMOS	38/100	38/95	19 400	1.04	Figure 3C
5	pMOS/tBOS	38/38	38/38	10 800	1.05	Figure 3E
6	pMOS/tBOS	38/100	38/99	19 000	1.04	Figure 3F
7	tBOS/pMS	38/38	38/41	10 800	1.20	Figure 4B
8	tBOS/pMS	38/100	38/105	16 600	1.22	Figure 4C

[a] In toluene at −15 °C; conversion = ca. 100% for each monomer; see the captions for Figures 1, 3, and 4 for the details of the reaction conditions. [b] A indicates the monomer that was first polymerized into a living polymer from which the second monomer B is polymerized. [c] Shown in the degree of polymerization for each segment. [d] Calculated from the ratio of the initial concentrations of the monomers and hydrogen iodide (=[monomer]$_0$/[HI]$_0$). [e] By ^{1}H NMR spectroscopy. [f] By size-exclusion chromatography; polystyrene calibration.

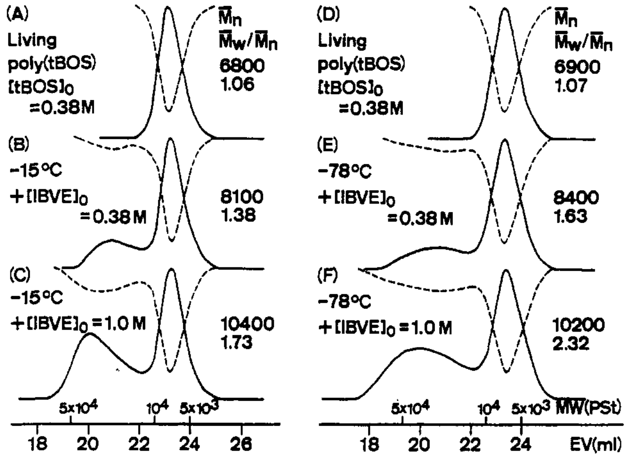


Figure 2. Polymer MWDs in the tBOS–IBVE block polymerization in toluene: (A and D) living poly(tBOS) formed at −15 °C; (B and C) block polymers from prepolymer A at −15 °C; (E and F) block polymers from prepolymer D at −78 °C. [HI]$_0$ = 10 mM, [ZnI$_2$]$_0$ = 5.0 mM; conversions are ca. 100% for both monomers. See the following table for other reaction conditions. (—) RI; (- - -) UV at 254 nm.

sample	first stage monomer (M)	first stage time	second stage monomer (M)	second stage time
A	tBOS (0.38)	19 h		
B	tBOS (0.38)	19 h	IBVE (0.38)	5 min
C	tBOS (0.38)	19 h	IBVE (1.0)	5 min
D	tBOS (0.38)	19 h		
E	tBOS (0.38)	19 h	IBVE (0.38)	12 h
F	tBOS (0.39)	19 h	IBVE (1.0)	12 h

The added IBVE was quantitatively polymerized in a few minutes. However, the polymers exhibited bimodal MWDs where the major fraction had a molecular weight nearly the same as that of the living tBOS prepolymer (Figure 2B,C). Both higher and lower peaks had ultraviolet absorptions due to the tBOS repeat units, and the product is most likely a mixture of a tBOS–IBVE block copolymer and a homopolymer of tBOS. Similar results have been obtained for the HI/ZnI$_2$-mediated block copolymerization of pMOS and IBVE starting from pMOS.[9]

In an attempt to improve the blocking efficiency, another series of the tBOS–IBVE polymerization from tBOS was carried out (Figures 2D–F), where the addition and polymerization of IBVE (the second monomer) were carried out at −78 °C; living tBOS prepolymer was prepared at −15 °C as described above.[4] Although the second-stage polymerization of IBVE was indeed much slower and quantitative (100% conversion after 12 h), the final products still showed bimodal MWDs that were similar to those obtained at −15 °C. According to the MWD by ultraviolet detection, the proportion of the living poly(tBOS) chains that reacted with the added IBVE did not vary with temperature for the second-stage polymerization [ca. 20% for −15 °C (Figure 2B,E); ca. 30% for −78 °C (Figures 2C,F)].

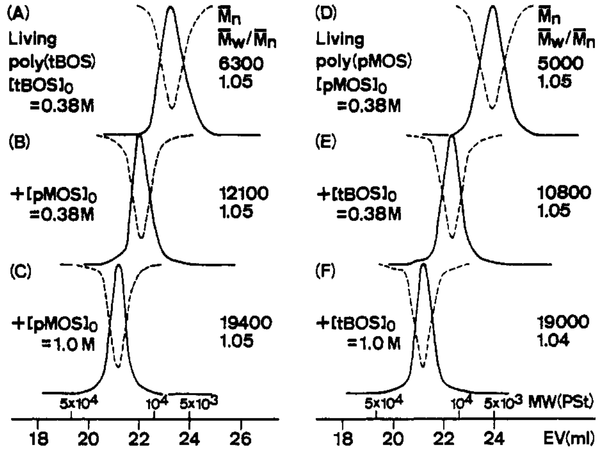


Figure 3. Polymer MWDs in the tBOS–pMOS block polymerizations in toluene at −15 °C: (A) living poly(tBOS); (B and C) block polymers from prepolymer A; (D) living poly(pMOS); (E and F) block polymers from prepolymer D. [HI]$_0$ = 10 mM, [ZnI$_2$]$_0$ = 5.0 mM; conversions are ca. 100% for both monomers. See the following table for other reaction conditions. (—) RI; (- - -) UV at 254 nm.

sample	first stage monomer (M)	first stage time	second stage monomer (M)	second stage time
A	tBOS (0.38)	19 h		
B	tBOS (0.38)	19 h	pMOS (0.38)	25 h
C	tBOS (0.38)	19 h	pMOS (1.0)	25 h
D	pMOS (0.38)	100 min		
E	pMOS (0.38)	100 min	tBOS (0.38)	45 h
F	pMOS (0.38)	100 min	tBOS (1.0)	45 h

As proposed in the previous paper,[9] the formation of polymers with bimodal MWDs is due to the difference in structure and reactivity between tBOS and IBVE and not due to a partial deactivation of the living prepolymer of tBOS. It was therefore revealed that the block copolymerizations of a vinyl ether and a styrene derivative must be initiated from the former, which is more reactive.

Block Copolymerization of tBOS and pMOS. In the living cationic polymerization with HI/ZnI$_2$, the reactivity of tBOS is similar to that of pMOS,[6] as expected from their similarity in structure. The similar reactivities suggest that sequential block copolymerizations of these styrenic monomers may be started from either of them, and this expectation was indeed corroborated experimentally (Figure 3).

The HI/ZnI$_2$ system gives living polymers of very narrow MWDs ($\bar{M}_w/\bar{M}_w \le 1.05$) from both tBOS and pMOS in toluene at −15 °C (parts A and D of Figure 3, respectively).[4,6] Addition of the second monomer (at two concentrations; without an additional dose of ZnI$_2$) induced quantitative polymerizations to afford block copolymers whose MWDs were as narrow as those of the starting living polymers (Figure 3). The second-phase reaction was slightly faster with pMOS than with tBOS. According to ^{1}H NMR analysis (Table I, entries 3–6), the molecular weights and compositions of the products are in agreement with the values calculated from the feed ratio of tBOS and pMOS (independent of the reaction sequence). Thus, the

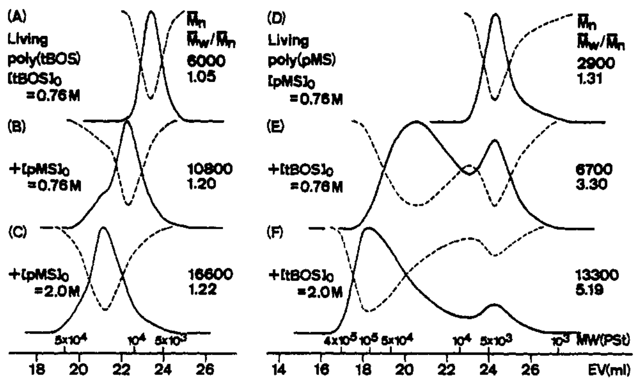


Figure 4. Polymer MWDs in the tBOS–pMS block polymerizations in toluene at −15 °C: (A) living poly(tBOS); (B and C) block polymers from prepolymer A; (D) living poly(pMS); (E and F) block polymers from prepolymer D. (A–C) $[HI]_0$ = 20 mM, $[ZnI_2]_0$ = 5.0 mM (+$[ZnCl_2]_0$ = 100 mM for the second stage in B and C); (D–F) $[HI]_0$ = 20 mM, $[ZnCl_2]_0$ = 100 mM; conversions are ca. 100% for all monomers. See the following table for other reaction conditions. (—) RI; (- - -) UV at 254 nm.

	frist stage		second stage	
sample	monomer (M)	time	monomer (M)	time
A	tBOS (0.76)	3 h		
B	tBOS (0.76)	3 h	pMS (0.76)	340 h
C	tBOS (0.76)	3 h	pMS (2.0)	340 h
D	pMS (2.0)	26 h		
E	pMS (2.0)	26 h	tBOS (0.76)	18 h
F	pMS (2.0)	26 h	tBOS (2.0)	18 h

tBOS–pMOS block copolymerization with HI/ZnI_2 is "reversible"; i.e., it may be started from either tBOS or pMOS without any adverse effect.

Block Copolymerization of tBOS and pMS. Because of its lower reactivity, living cationic polymerization of pMS is more difficult than those of tBOS and pMOS and has been achieved only recently with use of hydrogen iodide (20 mM) coupled with a large amount of $ZnCl_2$ (100 mM).[10] As pointed out above, it is obvious that block copolymerizations of pMS must be initiated from a more reactive comonomer. Therefore, tBOS was first polymerized by HI/ZnI_2 (20/5.0 mM) in toluene at −15 °C,[4] and then pMS was added to a resulting solution of living poly(tBOS) (Figure 4A). Although the added pMS was hardly polymerized at this stage, a slow but quantitative polymerization ensued on addition of a large amount of $ZnCl_2$ (100 mM); quantitative pMS conversion was reached after 2 weeks (340 h). The MWDs of the final products (Figure 4B,C) shifted toward higher molecular weight and were fairly narrow, though slightly broader than that of the living tBOS prepolymer. The compositions of the polymers were in good agreement with the feed molelar ratios of tBOS and pMS (Table I, entries 7 and 8), according to ^1H NMR analysis.

An attempt of block copolymerization of tBOS from living poly(pMS), in toluene at −15 °C with the $HI/ZnCl_2$ (20/100 mM) system, resulted in failure (Figure 4D–F). The polymerization of added tBOS was indeed quantitative, but the polymers had bimodal MWDs.

Thus, a more reactive monomer must be polymerized first even in block copolymerizations between styrene derivatives, if the reactivities of the comonomers considerably differ from each other.

Acidolysis of tBOS-Based Block Copolymers: Synthesis of Amphiphilic Macromolecules with a Poly(*p*-vinylphenol) Segment. Acidolysis of the tBOS-based block copolymers with hydrobromic acid was carried out in 1,4-dioxane to convert the poly(tBOS) segment into a poly(*p*-vinylphenol) chain (see under Experimental Section).[1b,4] Four amphiphilic block polymers (**4**–**7**) were thus prepared; note that **6** and **7** consist of the same segments but have opposite segmental sequences.

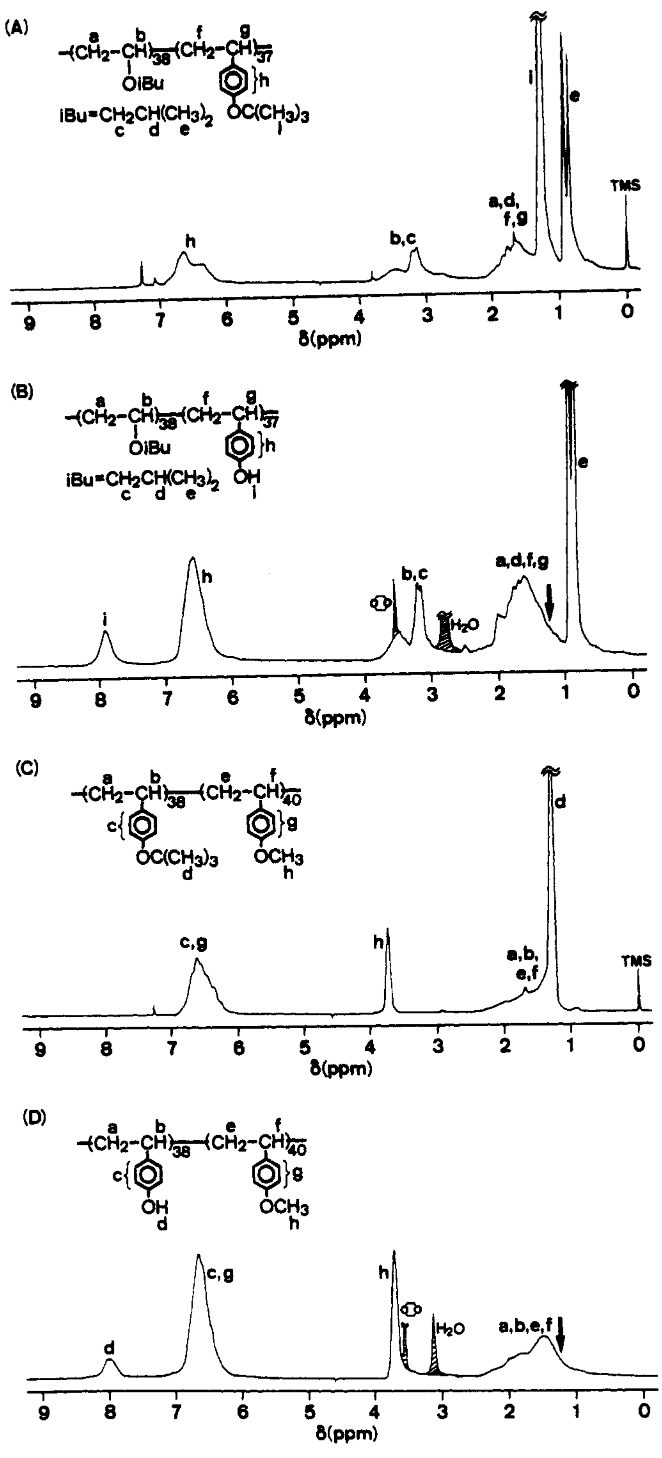


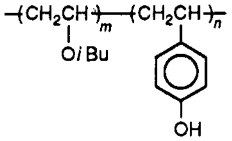
Figure 5. ^1H NMR spectra in $CDCl_3$ (A and C) and $(CD_3)_2CO$ (B and D): (A) poly(IBVE-*b*-tBOS), IBVE/tBOS = 38/37 (segment DP), the sample shown in Figure 1B; (B) acidolysis product from sample A; (C) poly(tBOS-*b*-pMOS), tBOS/pMOS = 38/40 (segment DP), the sample shown in Figure 3B; (D) acidolysis product from sample C. The vertical arrows in parts B and D indicate the position of the methyl resonance of the pendant *tert*-butyl group.

Figure 5 shows ^1H NMR spectra of block copolymers of tBOS with IBVE and pMOS (Table I, entries 1 and 3, respectively) and of their acidolysis products. In the ^1H NMR spectra obtained after the acidolysis (Figure 5B,D) the methyl resonance of the *tert*-butoxyl group at 1.3 ppm was completely absent (cf. Figure 5A,C for the polymers before the acidolysis), and the phenolic protons' signals

Table II
Solubility of tBOS-Based AB Block Copolymers before and after Acidolysis[a]

	block copolymer		solvent						
entry[b]	monomers[c]	segment DP[d]	1,4-dioxane	benzene	CH_2Cl_2	CH_3OH	$H_2O(OH^-)$[e]	H_2O	$n\text{-}C_6H_{14}$
A	tBOS/IBVE	38/38, 100/38	O [O]	O [X]	O [X]	X [O]	X [O]	X [X]	X [X]
B	tBOS/pMOS	38/38, 100/38	O [O]	O [X]	O [X]	X [O]	X [X]	X [X]	X [X]
C	tBOS/pMOS	38/100	O [O]	O [X]	O [X]	X [X]	X [X]	X [X]	X [X]
D	tBOS/pMS	38/38	O [O]	·O [X]	O [X]	X [O]	X [X]	X [X]	X [X]
E	tBOS/pMS	38/100	O [O]	O [X]	O [X]	X [X]	X [X]	X [X]	X [X]

[a] O, soluble; X, insoluble. At room temperature, ca. 1 wt %. Symbols in brackets indicate the solubility after acidolysis. [b] Entry numbers in Table I: (A) 1 and 2; (B) 3, 5, and 6; (C) 4; (D) 7; (E) 8. [c] Not indicating the monomer addition sequence in the synthesis; cf. Table I. [d] Shown, for simplicity, with the calculated values, which are very close to the observed (see Table I). [e] Aqueous NaOH solution (10%, w/v).



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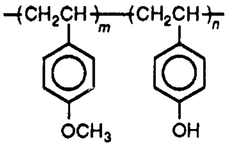

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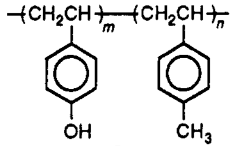

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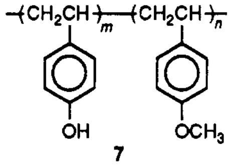

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appeared around 8 ppm. Additional NMR peaks indicative of byproducts were absent. Similarly, the acidolysis of the other samples shown in Table I was clean and quantitative.

Solubilities of the block copolymers were considerably changed upon the acidolysis, as Table II summarizes. Independent of compositions, for example, all the starting block copolymers with poly(tBOS) segments were soluble in 1,4-dioxane, benzene, and dichloromethane but were insoluble in methanol, water, and n-hexane. After the acidolysis, in contrast, the deprotected block copolymers were invariably insoluble in benzene and dichloromethane, though still soluble in 1,4-dioxane. Also upon the acidolysis, the block polymers of tBOS with IBVE became soluble in methanol and an alkali solution (e.g., Table II, entry A), whereas those of tBOS with pMOS and pMS (Table II, entries B and D) became soluble in methanol, if the tBOS (i.e., p-vinylphenol) units are in molar excess.

These variations in solubility characteristics show not only that the acidolysis proceeded quantitatively but also that the polymers were free from homopolymers. The block copolymers thus obtained are new nonionic amphiphilic macromolecules (polar/nonpolar block copolymers) that contain hard and polar p-vinylphenol segments and thereby differ from the vinyl ether based counterparts with flexible segments.[13]

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Registry No. (tBOS)(IBVE) (block copolymer), 132981-56-7; (tBOS)(pMOS) (block copolymer), 132981-57-8; (tBOS)(pMS) (block copolymer), 132981-58-9; HI, 10034-85-2; $ZnCl_2$, 7646-85-7; ZnI_2, 10139-47-6.