Selective Living Anionic Polymerization of a Novel Bifunctional Monomer 4-(Vinylphenyl)-1-butene and the Preparation of Uniform Size Functional Polymers and Amphiphilic Block Copolymers

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ABSTRACT: A novel bifunctional monomer, namely, 4-(vinylphenyl)-1-butene (VSt), was prepared by the coupling reaction between vinylbenzyl chloride and allylmagnesium chloride with a high yield (93%) and monomer purity. This monomer contains both a styrene type and a 1-butene type C═C double bond. The former double bond can be selectively polymerized by anionic polymerization to generate a polymer with a polystyrene [poly(St)] backbone and functional butenyl side chains. The effects of the initiator, temperature, and solvent were investigated, and the optimum conditions for the selective living anionic polymerization of this monomer were determined. Using *n*-BuLi as initiator, in a mixture of toluene and tetrahydrofuran (5:1−2:1), at −40 °C, VSt could undergo anionic polymerization in a living manner without cross-linking and any other side reactions. The polymer thus obtained possesses a controlled molecular weight and a very narrow molecular weight distribution ($M_w/M_n = 1.03-1.05$). The quantitative presence of the unreacted 1-butene type C═C double bonds was verified by ^{1}H NMR and FT-IR. The block copolymerization of VSt and St could also proceed smoothly in the polymerization sequence VSt followed by St, or vice versa, to generate a well-defined block copolymer with a controlled molecular weight and composition and a very narrow molecular weight distribution ($M_w/M_n = 1.03-1.07$). The C═C double bonds of the side chains of poly(VSt) were further reacted first with 9-borabicyclo[3.3.1]nonane (9-BBN), followed by the addition of sodium hydroxide and hydrogen peroxide. This procedure generated a uniform size hydrophilic functional polymer, poly(4-hydroxybutylstyrene), without destroying the main-chain structure of the polymer. This hydroxylation method was also applied to the block copolymer of VSt and St, and a well-defined amphiphilic block copolymer, containing both the hydrophilic poly(4-hydroxybutylstyrene) and the hydrophobic poly(St) segments, was obtained.

Introduction

Tremendous progress was achieved in the living polymerizations over the past two decades.[1−6] These well-established techniques allow to control the primary structure of the polymers, e.g., the molecular weight, molecular weight distribution (MWD), sequence distribution, stereoregularity, chain-end structures, and branching. The incorporation of functional groups into the polymer chains can greatly improve their properties, such as hydrophilicity, hydrophobicity, biocompatibility, adhesion, etc., thus providing polymers with additional useful characteristics. Therefore, the application of living polymerization methods to functional monomers is a route to high-performance polymers with well-defined molecular architectures.

Well-defined functional polymers have been prepared by combining a protection method with the living anionic polymerization technique.[7−9] The functional group of the monomer was first masked with a suitable group. Then, this protected monomer was subjected to anionic polymerization. Finally, the protecting group was removed under suitable conditions. Compared to this three-step synthetic procedure, the selective living polymerization method of a bifunctional monomer suggested in this paper is a more convenient route to functional polymers. If a monomer contains two functional groups with different polymerizibilities, one of them can be selectively polymerized under certain conditions, using a living polymerization method, without the interference of the other functional group. This one-step living polymerization process can generate a uniform size functional polymer with a functional group in each of its repeating units. For instance, the bifunctional monomer 4-(vinylphenyl)-1-butene (VSt, 1 in Scheme 1), prepared via the coupling reaction between vinylbenzyl chloride (VBC) and allylmagnesium chloride, contains two C═C double bonds: one is directly connected to the benzene ring, and the other one is separated from the benzene ring by an ethyl group. The latter bond cannot undergo anionic polymerization because ethyl is an electron-donating group. In contrast, the former can be subjected to anionic polymerization because the benzene ring stalilizes the propagating carbanion. Therefore, if the polymerization conditions are carefully selected, the selective anionic polymerization of VSt can generate a functional polymer with a controlled molecular weight, a narrow MWD, and a C═C double bond in each of its repeating units [poly(VSt), 2 in Scheme 1]. The latter double bonds can be further reacted with numerous reagents, such as 9-borabicyclo[3.3.1]nonane (9-BBN),[10] dimethylchlorosilane [H−Si$(CH_3)_2$Cl],[11] RCOOOH, etc., to generate other new uniform size functional polymers. In the present paper, the new monomer VSt was first prepared. Then, the effects of the initiator, solvent, and temperature on the selective anionic polymerization of VSt were investigated, and the optimum conditions to obtain a uniform size functional poly(VSt) were determined. Further, the resulting poly(VSt) was reacted with 9-BBN, and this was followed by the addition of sodium hydroxide and

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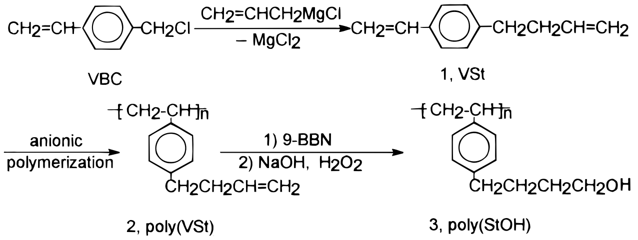
Scheme 1



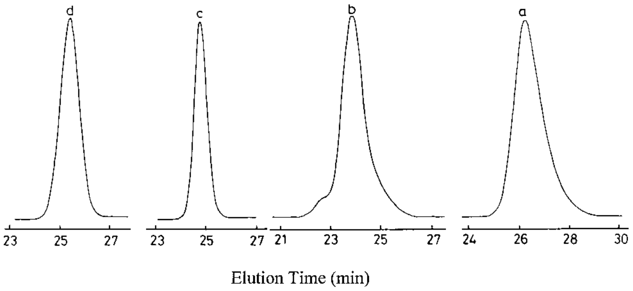


Figure 1. GPC traces of poly(VSt)s. (a) PVSt-1 (Table 1, $M_n = 3820$, $M_w/M_n = 1.31$) prepared in THF at −70 °C. (b) PVSt-6 ($M_n = 17\ 600$, $M_w/M_n = 1.32$) prepared in toluene at 20 °C in the presence of a trace amount of THF ([THF] = [n-BuLi]$_0$ = 24.3 mM). (c) PVSt-17 ($M_n = 15\ 200$, $M_w/M_n = 1.03$) prepared in a mixture of toluene and THF (2:1) at −40 °C. (d) Poly(St) standard (Pressure Chemical, lot no. 8b; $M_n = 10\ 000$, $M_w/M_n < 1.06$).

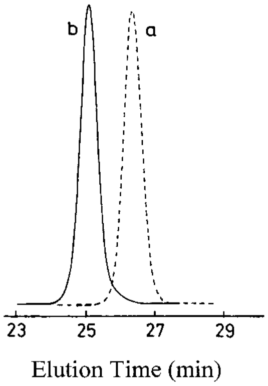


Figure 2. GPC traces of poly(VSt)s obtained by two monomer addition experiments. (a) First monomer addition, $M_n = 5480$, $M_w/M_n = 1.03$ ([n-BuLi]$_0$ = 18.2 mM, [VSt]$_0$ = 0.610 M, Tol/THF = 2/1). (b) Second monomer addition, $M_n = 11\ 100$, $M_w/M_n = 1.06$.

hydrogen peroxide. This hydroxylation process generated a new hydrophilic polymer, poly(4-hydroxybutylstyrene) [poly(StOH), 3 in Scheme 1]. The anionic block copolymerization of VSt and St was also carried out, and a well-defined block copolymer with a controlled molecular weight and composition and a very narrow MWD was obtained. The hydroxylation of the block copolymer generated another uniform size block copolymer with poly(St) hydrophobic and poly(StOH) hydrophilic segments.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried with CaH$_2$ under reflux for more than 24 h, distilled, and distilled again from a solution of sodium naphthalenide just before use. Toluene was washed with concentrated sulfuric acid and then with water, dried with MgSO$_4$, distilled over CaH$_2$, and finally distilled from a n-BuLi solution. Hexane was first dried and distilled over CaH$_2$ and then distilled from a solution of n-BuLi. Vinylbenzyl chloride (VBC; Aldrich, 97%) was dried with CaH$_2$ and distilled under reduced pressure. Styrene (St; Aldrich, 99%) was washed with 10% aqueous NaOH solution and then with water, dried overnight with MgSO$_4$, distilled over CaH$_2$, and finally distilled in the presence of phenylmagnesium chloride prior to polymerization. n-BuLi (Aldrich, 1.6 M solution in hexane) and *sec*-BuLi (Aldrich, 1.3 M solution in cyclohexane) were diluted with purified hexane. Sodium naphthalenide was prepared by reacting a small excess amount of naphthalene with sodium metal in THF at room temperature. Allylmagnesium chloride (AMC; Aldrich, 2.0 M solution in THF), 9-borabicyclo[3.3.1]nonane (9-BBN; Aldrich, 0.5 M solution in THF), and hydrogen peroxide (H$_2$O$_2$; Fisher, 30 wt % aqueous solution) were used as received.

Synthesis of 4-(Vinylphenyl)-1-butene (VSt). VSt was prepared through the coupling reaction between VBC and AMC. A 1000 mL round-bottom flask, equipped with a condenser, a paddle stirrer, and a dropping funnel with a pressure-equalization arm, was degassed and heated under reduced pressure. To this flask, 170 mL of THF solution of AMC (0.340 mol) was carefully added under the protection of N$_2$. Further, this solution was diluted by adding 100 mL of purified THF and cooled to 0 °C. Then, 50.0 g (0.318 mol) of VBC was dropwise added in 1.5 h with stirring, and the stirring was continued for an additional 2.5 h. After a saturated aqueous solution of NH$_4$Cl was added slowly, the mixture was washed three times with water, evaporated to remove the THF, and distilled under reduced pressure (bp: 43 °C/0.2 Torr, yield: 93% based on the amount of VBC employed). The monomer thus obtained was twice distilled in the presence of phenylmagnesium chloride prior to polymerization. As shown later in Figure 3A, the chemical shifts and their intensities in the ^{1}H NMR spectrum of the prepared VSt are consistent with its molecular structure.

Polymerization. The anionic homopolymerization of VSt and its block copolymerization with St were carried out in a round-bottom glass flask, under an overpressure of argon, with magnetic stirring, at selected temperatures. After the solvent(s) (THF, toluene, or both) were added with dry syringes, the flask was placed in a bath kept at a selected temperature, and an initiator (n-BuLi in hexane, *sec*-BuLi in cyclohexane, or sodium naphthalenide in THF) was added. The polymerization was induced by adding prechilled VSt. For the block copolymerization of VSt and St, the sequence VSt followed by St, or vice versa, was used. The system was quenched by adding a small amount of methanol, and the (co)polymer was precipitated by pouring the polymerization solution into a large amount of methanol. The (co)polymer thus obtained was washed with methanol and vacuum-dried at 40 °C for more than 24 h.

Hydroxylation of the (Co)polymer. The hydroxylation of poly(VSt) or poly(VSt-*b*-St) was carried out under the protection of N$_2$ in a round-bottom flask containing a magnetic stirring bar. For instance, 1.2 g of poly(VSt) (PVSt-16, Tables 1 and 3) was dissolved in 30 mL of purified THF. To this system, 23 mL of THF solution of 9-BBN (0.5 M) was added at room temperature, and the reaction was allowed to last 16 h. After 2.4 mL of aqueous solution of NaOH (5.0 M) was introduced into the system, the flask was cooled to 10 °C, and 4.0 mL of aqueous solution of H$_2$O$_2$ (30 wt %) was dropwise added carefully with a syringe to avoid the decomposition of H$_2$O$_2$ caused by a temperature increase.[10] Then, the stirring was continued for an additional 4 h at room temperature. After the system was concentrated by evaporation to about 20 mL, the polymer was precipitated by pouring the polymer solution into a large amount of a mixture of water and methanol (9:1), washed with water and then with methanol, and finally vacuum-dried at 40 °C for 24 h.

Measurements. ^{1}H NMR spectra were recorded in CDCl$_3$ or 1,4-dioxane-d_8 on an INOVA-400 spectrometer. M_n and M_w/M_n of the polymer were determined by gel permeation chromatography (GPC) on the basis of a polystyrene calibration curve. The GPC measurements were carried out using THF as solvent, at 30 °C, at a 1.0 mL/min flow rate and a 1.0 cm/min chart speed. Three polystyrene gel columns (Waters, 7.8

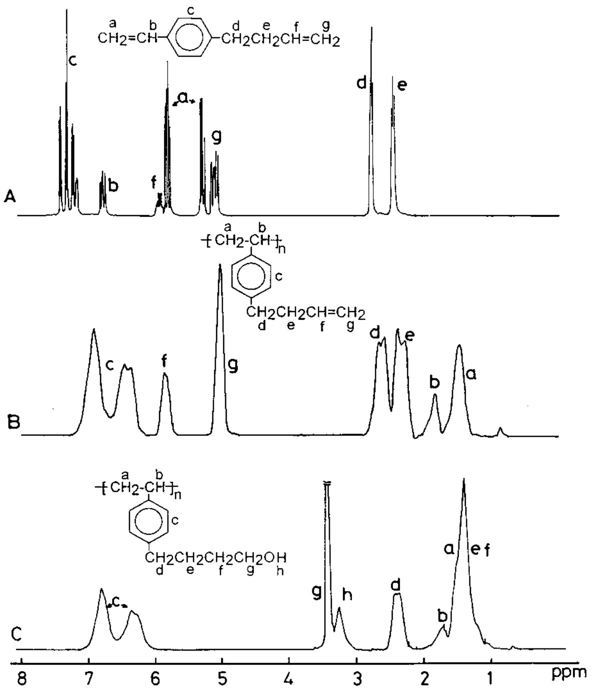


Figure 3. ^{1}H NMR spectra of VSt (A; in $CDCl_3$), poly(VSt) (B; in $CDCl_3$; see PVSt-16 in Table 1), and its hydroxylate poly-(StOH) (C; in 1,4-dioxane-d_8, see PStOH-16 in Table 3).

× 300 mm; one HR 5E, part no. 44228, one Linear, part no. 10681, and one HR 4E, part no. 44240) were used, which were connected to a Waters 515 precision pump. The FT-IR spectra were recorded on a Perkin-Elmer 1760-X spectrometer using a film prepared from a 1,4-dioxane [for poly(VSt)] or a THF [for poly(StOH)] solution.

Results and Discussion

Selective Living Anionic Polymerization of VSt. It is well-known that the living anionic polymerization of St can proceed smoothly either in a polar solvent, such as THF, at a low temperature, or in a nonpolar solvent, such as benzene and toluene, at room temperature. Because VSt has a molecular structure similar to that of St, its anionic polymerization was first examined under the optimum conditions determined for St. When the polymerization was carried out in THF, at −70 °C, using *n*-BuLi as initiator, poly(VSt) with a broader MWD was obtained quantitatively (PVSt-1 and 2 in Table 1, M_w/M_n = 1.31−1.36). As shown in Figure 1a, the GPC chromatogram of the obtained polymer exhibits an unsymmetrical peak with a heavy tailing in the low molecular weight region. When the initiator *n*-BuLi was replaced with sodium naphthalenide, besides the above tailing, the resulting polymer possessed an even broader MWD (M_w/M_n = 1.58) and an uncontrolled molecular weight (PVSt-3). The above results indicate that a deactivation of the propagating sites occurred during the polymerization process. In this polar solvent (THF), the propagating carbanion has a very high reactivity and may deactivate by capturing a proton from the butenyl of VSt, especially from the two protons of the methylene directly connected to the benzene ring.

When the polymerization of VSt was carried out in a nonpolar solvent (toluene), at a high temperature (20 °C), using *sec*-BuLi or *n*-BuLi as initiator, only a trace amount of polymer was obtained (PVSt-4 and 5 in Table 1), which is quite different from that obtained via the anionic polymerization of St. Because of the high temperature and the low propagating rate in the nonpolar solvent, the side reaction of the initiator with the butenyl protons of VSt was dominant. When, however, a trace amount of THF ($[\mathrm{THF}] = [n\text{-BuLi}]_0$) was added to the latter system, the monomer was polymerized quantitatively (PVSt-6 in Table 1). Consequently, the introduction of THF into the nonpolar solvent is beneficial because it increases both the polymerization rate and the initiator efficiency. However, the initiator efficiency was still very low (20%), and in the GPC chromatogram of the obtained polymer, a shoulder appeared in the high molecular weight side (Figure 1b), which most likely represents a cross-linked polymer whose amount increased as the polymerization lasted longer. At the high temperature of 20 °C, the C═C double bond of the butenyl of VSt may also participate to some extent in the polymerization, resulting in the cross-linking side reaction.

The effect of the temperature on the selective anionic polymerization of VSt was investigated in toluene from 0 to −40 °C (PVSt-7−10), in the presence of a small amount of THF (Tol/THF = 40/1, volume ratio). As shown in Table 1, as the temperature decreased from 0 to −40 °C, the initiator efficiency increased from 32 to 54%, but the monomer conversion decreased from 89 to 35%. This means that the low temperature is beneficial in depressing the side reactions in the initiating period but also decreases the rate of the propagating reaction.

Keeping the temperature at −40 °C, the effect of the volume ratio of toluene and THF (Tol/THF) on the polymerization of VSt was investigated (PVSt-11−15 in Table 1). For the ratios Tol/THF = 10/1, 5/1, 2/1, 1/1 and 1/2, the best results were obtained in the range 5/1 to 2/1. As shown in Table 1, the monomer conversion was 100% in that range, the determined molecular weight was in good agreement with that calculated, and the MWD was very narrow (M_w/M_n = 1.03 and 1.04). In addition, by changing the feed amounts of the initiator and the monomer, uniform size poly(VSt)s with different molecular weights were prepared (PVSt-16−19 in Table 1). As shown in Figure 1c, the GPC chromatogram of the obtained polymer exhibits a very sharp and symmetrical peak (PVSt-17, M_n = 15 200, M_w/M_n = 1.03), comparable to that of the polystyrene standard (Figure 1d, M_n = 10 000, M_w/M_n < 1.06). The above results indicate that the anionic polymerization of VSt can proceed smoothly under the above conditions without side reactions either during the initiating or during the propagating period.

Two Monomer Addition Experiments. To identify the living nature of the anionic polymerization of VSt, two successive monomer addition experiments were carried out at −40 °C, for a ratio of Tol/THF of 2/1. The GPC results are presented in Figure 2. In the first stage, poly(VSt) with a very narrow MWD (peak a, M_n = 5480, M_w/M_n = 1.03) was obtained. After the same amount of VSt was added to the system, the GPC peak shifted toward the higher molecular weight, but the MWD remained narrow (peak b, M_n = 11 100, M_w/M_n = 1.06), and no precursor polymer remained. The above results clearly indicate that the anionic polymerization of VSt proceeded in a living manner.

Parts A and B of Figure 3 depict the ^{1}H NMR spectra of VSt and its polymer, respectively. After polymerization, peaks a and b in Figure 3A due to CH_2═ and ═CH− of the styrene type vinyl disappeared completely, and two new absorptions corresponding to $-CH_2-$ and

Table 1. Anionic Polymerization of VSt

no.	initiator (mM)	$[VSt]_0$ (M)	time (min)	solvent[a]	temp (°C)	conv (%)	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]	f[d] (%)
PVSt-1	*n*-BuLi 21.1	0.523	40	THF	−70	100	3.97	3.82	1.31	100
PVSt-2	*n*-BuLi 6.8	0.723	40	THF	−70	100	16.8	22.1	1.36	76
PVSt-3	Na−Naph[e] 18.8	0.435	40	THF	−70	100	7.37	22.3	1.58	33
PVSt-4	*sec*-BuLi 21.1	0.523	40	Tol	20	*h*				
PVSt-5	*n*-BuLi 21.1	0.523	40	Tol	20	*h*				
PVSt-6	*n*-BuLi 24.3	0.523	40	Tol/THF[g]	20	100	3.45	17.6	1.32	20
PVSt-7	*n*-BuLi 24.3	0.523	40	Tol/THF = 40/1	0	89	3.08	9.63	1.15	32
PVSt-8	*n*-BuLi 24.3	0.523	40	Tol/THF = 40/1	−10	80	2.77	6.89	1.12	40
PVSt-9	*n*-BuLi 24.3	0.523	40	Tol/THF = 40/1	−20	51	1.79	3.89	1.11	46
PVSt-10	*n*-BuLi 24.3	0.523	40	Tol/THF = 40/1	−40	35	1.19	2.11	1.14	54
PVSt-11	*n*-BuLi 24.3	0.523	40	Tol/THF = 10/1	−40	82	2.84	5.08	1.13	56
PVSt-12	*n*-BuLi 20.0	0.497	40	Tol/THF = 5/1	−40	100	3.98	3.92	1.04	100
PVSt-13	*n*-BuLi 20.0	0.497	40	Tol/THF = 2/1	−40	100	3.98	3.88	1.03	100
PVSt-14	*n*-BuLi 20.0	0.497	40	Tol/THF = 1/1	−40	100	3.98	3.79	1.08	100
PVSt-15	*n*-BuLi 20.0	0.497	40	Tol/THF = 1/2	−40	100	3.98	4.12	1.17	100
PVSt-16	*n*-BuLi 7.4	0.516	60	Tol/THF = 2/1	−40	100	11.1	11.4	1.04	97
PVSt-17	*n*-BuLi 7.0	0.647	60	Tol/THF = 2/1	−40	100	14.6	15.2	1.03	96
PVSt-18	*n*-BuLi 6.6	0.651	60	Tol/THF = 2/1	−40	100	15.6	17.1	1.04	91
PVSt-19	*n*-BuLi 6.9	0.966	80	Tol/THF = 2/1	−40	100	22.1	24.8	1.07	89

[a] Tol = toluene; THF = tetrahydrofuran; Tol/THF = the volume ratio of the two solvents. [b] Calculated M_n. [c] Determined by GPC on the basis of a polystyrene calibration curve. [d] Initiator efficiency. [e] Sodium naphthalenide. [g] [THF] = $[n\text{-BuLi}]_0$ = 24.3 mM. [h] Trace.

Table 2. Anionic Block Copolymerization of VSt and St[a]

no.	block sequence	$[n\text{-BuLi}]_0$ (mM)	$[M_1]_0$ (M)	$[M_2]_0$ (M)	first step $10^{-3}M_k$[b]	first step $10^{-3}M_n$[c]	first step M_w/M_n[c]	second step $10^{-3}M_k$[b]	second step $10^{-3}M_n$[c]	second step M_w/M_n[c]
VbS-1	VSt → St	8.90	0.447	0.566	7.99	8.29	1.04	14.6	15.3	1.04
VbS-2	VSt → St	7.00	0.249	0.876	5.68	5.92	1.04	18.7	19.5	1.03
SbV-1	St → VSt	15.6	0.601	0.435	4.06	4.39	1.06	8.47	7.96	1.07
SbV-2	St → VSt	10.2	0.601	0.220	6.18	6.40	1.05	9.59	10.5	1.06

[a] The anionic block copolymerization was carried out in a mixture of toluene and THF (2:1) at −40 °C. The polymerization times for VSt and St were 60 and 40 min, respectively. After the polymerization of the first monomer, a trace amount of polymer solution (ca. 0.2 mL) was taken out for GPC measurement. Then, the second monomer was successively added. [b] Calculated M_n. [c] Determined by GPC on the basis of a polystyrene calibration curve.

Table 3. Hydroxylation of Poly(VSt) and Poly(VSt-*b*-St)[a]

no.	polymer[b]	C=C[c] (mmol)	9-BBN[d] (mmol)	NaOH[e] (mmol)	H_2O_2[f] (mmol)	functionality[g] (%)
PStOH-12	PVSt-12	6.3	13	13	39	100
PStOH-16	PVSt-16	7.6	12	12	36	100
h-VbS-1	VbS-1	5.0	10	10	30	100
h-SbV-1	SbV-1	7.0	14	14	42	100

[a] The reaction between the C=C double bond and 9-BBN was carried out in THF at room temperature with magnetic stirring for 16 h. Then, NaOH and H_2O_2 were added successively, and the reaction was allowed to last 4 h. [b] 4.0 g/100 mL of THF solution. [c] The amount of C=C double bond in the (co)polymer. [d] 0.5 M THF solution. [e] 5.0 M aqueous solution. [f] 30 wt % aqueous solution. [g] Determined by ^{1}H NMR.

Table 4. Solubility before and after Hydroxylation[a]

no.	hexane	benzene	$CHCl_3$	THF	dioxane	acetone	CH_3OH	C_2H_5OH	H_2O
PVSt-16	S	S	S	S	S	S	I	I	I
PStOH-16	I	I	I	S	S	S	S	S	I
VbS-1	S	S	S	S	S	S	I	I	I
h-VbS-1	I	W	D	S	S	S	W	W	I

[a] The experiment was carried out at room temperature. The amounts of (co)polymer and solvent were 0.03 g and 1.0 mL, respectively. S = soluble; D = dissolved slowly; W = wetting; I = insoluble. h- = hydroxylate of VbS-1.

−CH− of poly(VSt) main chain emerged at 1.41 and 1.79 ppm, respectively. On the other hand, the peaks f and g due to −CH= and =CH_2 of the butenyl remained unreacted after polymerization. Furthermore, as shown later in Table 4, the resulting poly(VSt) is soluble in a number of solvents, such as hexane, benzene, chloroform, THF, 1,4-dioxane, acetone, etc. Therefore, one can conclude that the styrene type C=C double bond of VSt was selectively polymerized, that no cross-linking reaction occurred during polymerization, and that the polymer thus obtained is a functional polymer possessing a reactive C=C double bond in each of its repeating units.

Anionic Block Copolymerization of VSt and St. The block copolymerization of VSt and St was carried out under conditions similar to those for the homopolymerization of VSt, using the polymerization sequence VSt−St, or vice versa. As shown in Table 2, well-defined block copolymers were obtained in each case, regardless of the polymerization sequence. As illustrated in Figure 4, the first step anionic polymerization of VSt generated a living polymer with a very narrow MWD (peak a, M_n = 5920, M_w/M_n = 1.04). Upon the subsequent addition of St, the polymerization continued quantitatively. The block copolymer thus obtained possessed a higher molecular weight than its precursor, and its MWD re-

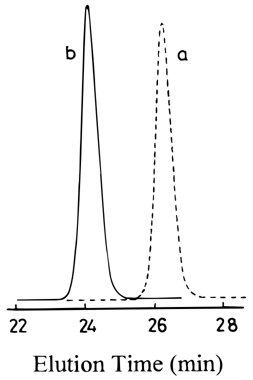


Figure 4. GPC traces of the block copolymer of VSt and St (peak b, VbS-2 in Table 2, M_n = 19 500, M_w/M_n = 1.03) and its living poly(VSt) precursor (peak a, M_n = 5920, M_w/M_n = 1.04).

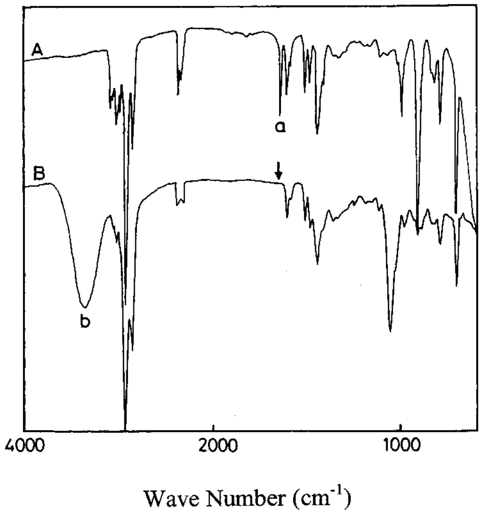


Figure 5. FT-IR spectra of poly(VSt) (A, PVSt-16 in Table 1) and its hydroxylate poly(StOH) (B, PStOH-16 in Table 3). Peaks A−a and B−b correspond to C=C double bonds in poly(VSt) side chains and hydroxy groups in poly(StOH) side chains, respectively.

mained very narrow (peak b, M_n = 19 500, M_w/M_n = 1.03). In addition, the molecular weight and the composition of each of the block copolymers can be well-controlled. Therefore, the anionic block copolymerization of VSt and St not only generated well-defined block copolymer but also demonstrated the living polymerization characteristics of VSt.

Hydroxylation of the (Co)polymers. The reaction of the C=C double bond with 9-BBN, followed by the addition of sodium hydroxide and hydrogen peroxide, has been often used for the hydroxylation of compounds containing C=C bonds. For instance, Chung et al.[10a] investigated systematically the hydroboration of polydienes and prepared well-defined functional hydrocarbon polymers. Mao et al.[10d] applied this hydroboration to a block copolymer of St and isoprene, and the product was further used to prepare liquid crystal−coil diblock copolymers. In the present paper, this method was employed to prepare a novel hydrophilic polymer, poly(4-hydroxybutylstyrene) [poly(StOH)], by transforming the butenyl side chain of poly(VSt) to 4-hydroxybutyl (3 in Scheme 1). The application of this reaction to a block copolymer of VSt and St generated an amphiphilic block copolymer containing both poly(StOH) hydrophilic and poly(St) hydrophobic segments.

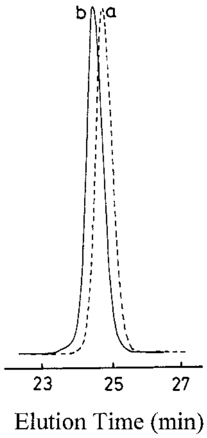


Figure 6. GPC traces of the block copolymer, poly(VSt-*b*-St) (peak a; VbS-1 in Table 2, M_n = 15 300, M_w/M_n = 1.04) and its hydroxylate (peak b; M_n = 16 200, M_w/M_n = 1.06).

As shown in Table 3, the hydroxylation was carried out in THF at room temperature. The C=C double bonds of the side chains of poly(VSt) were allowed to react with an excess of 9-BBN overnight, and subsequently, aqueous solutions of NaOH and H_2O_2 were added successively. The ^{1}H NMR spectra of the precursor poly(VSt) and its hydroxylate, poly(StOH), are presented in Figure 3, B and C, respectively. As above, the C=C double bond (peaks f and g in Figure 3B) of the butenyl remained unreacted after the polymerization of VSt. However, upon hydroxylation, these two peaks disappeared completely, and two new peaks emerged at 3.25 and 3.40 ppm (peaks h and g in Figure 3C), corresponding to −OH and $-CH_2O-$ of the 4-hydroxybutyl side chain of poly(StOH). This means that the butenyl side chains of poly(VSt) completely changed to 4-hydroxybutyl side chains. This result was also supported by the FT-IR measurements. As shown in Figure 5, the absorption (A−a; 1620 cm^{-1}) due to the C=C double bonds in poly(VSt) side chains disappeared completely after hydroxylation, and a broad band (B−b; 3100−3600 cm^{-1}) corresponding to the hydroxyl group of poly(StOH) appeared. For the hydroxylation of the block copolymers of VSt and St, similar ^{1}H NMR and FT-IR results were obtained.

To verify whether the main chain of poly(VSt) was not destroyed during hydroxylation, GPC measurements for the resulting polymers were carried out, but no MWD change was observed. For instance, the molecular weight of the block copolymer VbS-1 (Table 2) increased somewhat after hydroxylation (from M_n = 15 300 to M_n = 16 200) due to the addition of water to the C=C double bond of its side chain. However, its MWD remained unchanged, and the GPC chromatogram still exhibited a single, symmetrical peak (Figure 6). The above results clearly indicate that the poly(VSt) was changed to another functional polymer poly(StOH) and that this hydroxylation process has not affected the main chain of the polymer. For this reason, poly(StOH) is also a uniform size functional polymer.

Compared to their precursors, the hydroxylates of poly(VSt) and poly(VSt-*b*-St) exhibit different solubilities. As shown in Table 4, in contrast to poly(VSt), which is insoluble in methanol and ethanol, its hydroxylate is soluble in these polar solvents but insoluble in nonpolar solvents, such as hexane, benzene, chloroform, etc. On the other hand, because of the coexistence of hydrophilic poly(StOH) and hydrophobic poly(St) segments in the hydroxylate of the block copolymer, the resulting poly(StOH-*b*-St) is soluble in those solvents that are good solvents for both segments, such as THF, 1,4-dioxane, etc. It is, however, wetted by some nonpolar, such as benzene, and polar, such as alcohols, solvents.

Conclusions

A new bifunctional monomer 4-(vinylphenyl)-1-butene (VSt) was prepared, by the coupling reaction between vinylbenzyl chloride and allylmagnesium chloride, with a high yield (93%) and high purity. Its styrene type C═C double bond could be selectively polymerized by anionic polymerization to generate a polymer with a polystyrene [poly(St)] backbone and butenyl side chains. Using *n*-BuLi as initiator, in a mixture of toluene and tetrahydrofuran (5:1−2:1), at −40 °C, VSt could undergo anionic polymerization in a living manner without cross-linking or any other side reaction. The polymer thus obtained possesses a controlled molecular weight, a very narrow molecular weight distribution ($M_w/M_n = 1.03-1.05$), and an unreacted C═C double bond in each of its repeating units. A well-defined block copolymer of VSt and St with a controlled molecular weight and composition and a very narrow molecular weight distribution ($M_w/M_n = 1.03-1.07$) could also be obtained via the block copolymerization of the two monomers. The C═C double bonds of the side chains of poly(VSt) could be further reacted with 9-borabicyclo[3.3.1]nonane, followed by the addition of sodium hydroxide and hydrogen peroxide, to generate another uniform size hydrophilic functional polymer, poly(4-hydroxybutylstyrene). This hydroxylation process could also be applied to the block copolymer of VSt and St, and a well-defined amphiphilic block copolymer containing both the hydrophilic poly(4-hydroxybutylstyrene) and the hydrophobic poly(St) segments could be obtained.

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