Model Block−Graft Copolymer *via* Anionic Living Polymerization: Preparation and Characterization of [Poly((4-vinylphenyl)dimethylvinylsilane)-*graft*-polyisoprene]-*block*-polystyrene

Kazunori Se*

Department of Materials Science and Engineering, Faculty of Engineering,
Fukui University, Bunkyo 3-9-1, Fukui 910, Japan

Hiroki Yamazaki, Takeshi Shibamoto,[†] Atsushi Takano, and Teruo Fujimoto

Department of Chemistry, Faculty of Engineering, Nagaoka University of Technology,
Kamitomioka 1603-1, Nagaoka, Niigata 940-21, Japan

Received October 1, 1996; Revised Manuscript Received January 13, 1997[⊗]

ABSTRACT: A model graft copolymer that has well-defined length, number, and position of grafts was prepared *via* anionic living polymerization. (4-Vinylphenyl)dimethylvinylsilane (VS) was anionically polymerized by cumylcesium in THF at −78 °C for 20 min under a pressure of 10^{-5} mmHg, and subsequent addition of styrene (St) yielded a PVS-*b*-PSt block copolymer that could be used as a backbone molecule. PVS has a silylvinyl group on the side chain that converts chemical links between backbone and grafts. Isoprene (Is) was anionically polymerized to yield living polyisoprene, and the resultant $\mathrm{PIs^-Cs^+}$ and $\mathrm{PIs^-Li^+}$ solutions were added to THF and benzene solutions of PVS-*b*-PSt, respectively. After 24 h, backbone coupling was terminated to yield [poly((4-vinylphenyl)dimethylvinylsilane)-*graft*-polyisoprene]-*block*-polystyrene. The three graft copolymers were prepared. Molecular characterization was carried out by GPC measurement, osmometry, and sedimentation pattern. The M_n and M_w/M_n values of the backbone, grafts, and graft copolymers were determined. The number of grafts per backbone molecule was found to be $10._0$, $10._9$, and $12._5$ for the three graft copolymers, and the position of the grafts was set to the end of the backbone molecule. Spacing and its distribution of the graft points on a backbone molecule were also discussed. Three benzene-cast films formed clear microphase-separated structures, such as spherical and lamellar structures. The composition dependence on the morphology of the graft copolymers was found to differ from that of common block copolymers. These results suggest that the apparent volume fraction of grafts is much larger than the real volume fraction, because the grafts became crowded in the vicinity of the backbone molecule.

Introduction

Block copolymers and graft copolymers are thought to be chemically linked pairs of homopolymers. According to chemical bonding between different polymer species, under a segregation limit, block copolymers form a unique structure; namely a microphase-separated structure (MS structure).[1,2] The MS structure of block copolymers is far different from those of corresponding homopolymers and their blends, and details of the MS structure of block copolymers have been studied by numerous researchers,[3−6] including the present authors.[7,8] Furthermore, the relationship between MS structure and physical properties of block copolymers has been systematically studied in detail.[1−4]

In contrast, few studies have investigated the relationship between MS structure and physical properties of graft copolymers,[9] because well-defined graft copolymers have not been available.[10−12] Because of this, we create and employ a model graft copolymer, namely, a model in which the backbone has a narrow molecular weight distribution (MWD), the graft has a narrow MWD, the number of grafts per backbone molecule has a narrow distribution, and the position and spacing of grafts on a backbone are well-defined.[13−16] This graft copolymer is termed a block−graft copolymer because it is formed *via* a synthetic route of anionic living polymerization.

In the case of common graft copolymers, positions and spacing of grafts, which are attributable to a chemical link between the backbone and graft, are believed to be random. The positions and spacing of grafts constitute an essential factor for preparing well-defined graft copolymers. Thus, a block−graft copolymer must contain grafts that exist in a desirable position of the backbone molecule: a terminal or the central position. In order to prepare this block−graft copolymer, an AB-type block copolymer or an ABA-type block copolymer is first prepared, wherein the “A” polymer contains no functional groups that convert chemical links of grafts, and the “B” polymer contains these functional groups. Secondly, “C” polymers are attached as grafts to the “B” polymer of an AB-type or an ABA-type block copolymer to yield a block−graft copolymer.

More positive control of the structure of block−graft copolymers can be achieved by employing anionic rather than cationic or radical grafting mechanisms. A much better efficiency is possible when an anionic living mechanism is employed. In order to prepare such block−graft copolymers *via* anionic living polymerization, two approaches have generally been proposed, namely, a “grafting from” process (backbone initiation) and a “grafting onto” process (backbone coupling).[1,12,13] The first approach is exemplified by initiation of ethylene oxide by metalated poly(hydroxylstyrene). This

---

[*] To whom all correspondence should be addressed.

[†] Present address: Research & Development, Pola Cosmetics Co. Ltd., Kanagawaku, Yokohama 221, Japan.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

S0024-9297(96)01463-5 CCC: $14.00

backbone can be prepared by reacting poly(hydroxylstyrene) with cumylpotassium. The hydroxyl group reacts with cumylpotassium to generate a potassium hydroxide, thereby forming a macromolecular initiating species. However, precise control of the number and length of grafts appears to be difficult to achieve, because propagation from the macromolecular initiating species is more complex than that from initiators having low molecular weight. An experiment related to this phenomenon will be described elsewhere.

In contrast, the second approach (backbone coupling) is exemplified by a reaction of living polycarbanions with the backbone that bears the functional groups. This coupling technique has been used to prepare a four-armed star polymer; namely a coupling of four polystyryllithium with a 1,2-bis(methyldichlorosilyl)ethane.[17,18] This approach allows precise control of the number and length of grafts but is only applicable to a limited system.[1,12] In the present study, backbone coupling is investigated in detail in an effort to prepare and characterize [poly((4-vinylphenyl)dimethylvinylsilane)-*graft*-polyisoprene]-*block*-polystyrene block−graft copolymer, abbreviated as (PVS-*g*-PIs)-*b*-PSt.

Experimental Section

Reagents. *sec*-Butyllithium (*s*-BuLi) was prepared by reacting *sec*-butyl bromide with lithium in *n*-heptane. Cumylcesium ((cumyl)Cs) was prepared by reacting cumyl methyl ether and metal cesium in THF. The concentration of initiators was determined by titration with a standard HCl solution. Isoprene (Is) was dried over calcium hydride and sodium metal under reduced pressure and then purified by the addition of *n*-BuLi. Styrene (St) was dried over calcium hydride under reduced pressure, purified with octylbenzophenone−sodium,[19,20] and then diluted to approximately 15% with purified benzene. (4-Vinylphenyl)dimethylvinylsilane (VS) was prepared through a method described in another paper by the present authors.[15,21,22] The resultant VS was dried over calcium hydride under reduced pressure and purified with octylbenzophenone−sodium. Subsequently, VS was diluted with carefully purified solvents and was used for polymerization.

Benzene used for polymerization of isoprene and *n*-heptane used for dilution of the initiator were distilled with the addition of *n*-BuLi after conventional purification. THF used for polymerization of the backbone and for block−graft copolymers was dried with sodium metal, distilled in a vacuum with anthracene sodium, and then purified by distillation from a mixture of α-methylstyrene tetramer−sodium.

Polymerization. Poly((4-vinylphenyl)dimethylvinylsilane)-*block*-polystyrene (PVS-*b*-PSt) and polyisoprene (PIs) were prepared using an anionic living polymerization technique. Polymerization and the "grafting onto" process (backbone coupling) were carried out in a sealed glass apparatus under a pressure of 10^{-5} mmHg. The polymerization techniques were almost the same as those employed in previous studies conducted by the present authors.[19,20]

Molecular Characterization. Number average molecular weights (M_n) of the backbone, the graft, and the block−graft copolymer were determined in toluene at 30 °C using a Hewlett-Packard Type 502 high-speed membrane osmometer. ^{1}H nuclear magnetic resonance was measured in deuteriochloroform at 30 °C by using JEOL-GX270 FT-NMR spectrometer (JEOL Ltd.). Molecular weight distributions of the backbone, the graft, and the block−graft copolymer were tested by gel permeation chromatography (GPC, Model HLC 801A, Tosoh Ltd.) in THF using high-resolution columns (G5000H6, GMH-6, G4000H8: 7.5 mm i.d. × 60 cm, Tosoh Ltd.), and were tested by an analytical ultracentrifuge (Beckman, Spinco Model E) in THF at 25 °C.

Transmission Electron Microscopy. Block−graft copolymers were cast from a 5 w/w % benzene solution into thin films of approximately 0.2 mm thickness by gradually evaporating solvent at 25 °C. Benzene is a good solvent for the three constituent polymers. The resultant films were completely dried under a reduced pressure of 10^{-3}mmHg at 40 °C. The films, stained with a fixing reagent of osmium tetraoxide (OsO_4) were embedded in a resin and cut into ultrathin sections by an ultramicrotome. The morphology of these sections was examined using a Hitachi Type HU-12 transmission electron microscope.

Results and Discussion

Preparation of Model Block-Graft Copolymers. When preparing model block−graft copolymers, particular attention should be directed to the "B" monomer of the AB-type or ABA-type block copolymer that serves as the backbone. The "B" monomer must contain a functional group that converts the chemical link of the graft. For this reason, a new monomer, (4-vinylphenyl)-dimethylvinylsilane (VS), was employed as the "B" monomer; VS has two vinyl groups of a styryl group and a silylvinyl group. Although the silylvinyl group of VS is thought to be much less reactive than the styryl group of VS in a polar solvent,[22−24] both the vinyl groups are capable of polymerizing. When VS was allowed to react with (cumyl)Cs in THF under a high vacuum, which has been investigated in detail by the present authors,[15,21,22] the styryl group was selectively polymerized to yield the polymer which has the silylvinyl groups on the side chains. However, after chain propagation completely finished, the styryl living end of the polymer molecule was found to attach to the silylvinyl group on the side chain of another or the same polymer molecule. Hence, the corresponding GPC chromatogram showed double and/or triple peaks which correspond to a dimer and/or a trimer of the primary living molecules. That is to say, propagation of the styryl group of VS is believed to be in competition with the side reaction relating to the silylvinyl group of VS. In order to suppress this side reaction and to prepare PVS having a narrow MWD, VS should be polymerized for less than 30 min and subsequent termination of the living end should be carried out as soon as possible.

Using this VS as the "B" monomer, a model block−graft copolymer such as [poly((4-vinylphenyl)dimethylvinylsilane)-*graft*-polyisoprene]-*block*-polystyrene, (PVS-*g*-PIs)-*b*-PSt, was prepared through the following synthetic route of (1), (2), and (3).

$$\mathrm{PVS^-Cs^+} + \mathrm{St} \rightarrow \mathrm{PVS\text{-}}b\mathrm{\text{-}PSt} \tag{1}$$

$$\mathrm{Is} + \mathrm{(cumyl)Cs\ or\ }s\mathrm{\text{-}BuLi} \rightarrow \mathrm{PIs^-Cs^+\ or\ PIs^-Li^+} \tag{2}$$

$$\mathrm{PVS\text{-}}b\mathrm{\text{-}PSt} + \mathrm{PIs^-Cs^+\ or\ PIs^-Li^+} \rightarrow (\mathrm{PVS\text{-}}g\mathrm{\text{-}PIs})\text{-}b\text{-}\mathrm{PSt} \tag{3}$$

In (1), PVS-*b*-PSt block copolymer as the backbone was prepared in THF at −78 °C by the two-stage sequential addition of VS and styrene (St), using (cumyl)Cs as the initiator. Respective polymerization times of VS and St were 20 min and 1 h. The resultant polymer conversion rate was nearly 100%. As shown in Figure 1, the corresponding GPC chromatogram shows a sharp peak that has a small shoulder at the higher molecular weight side. This shoulder is believed to arise from the side reaction relating to the silylvinyl group, namely the styrylcesium of PVS-*b*-PSt^-Cs^+ living end attaching to the silylvinyl group of PVS block of another PVS-*b*-PSt^-Cs^+ living molecule.[22] In order to obtain pure PVS-*b*-PSt block copolymer without the dimer and trimer of the primary block copolymer, the product was fractionated with cyclohexane. Figure 1 shows a GPC chromatogram of the resultant PVS-*b*-PSt block copolymer for use as the backbone. The molecular

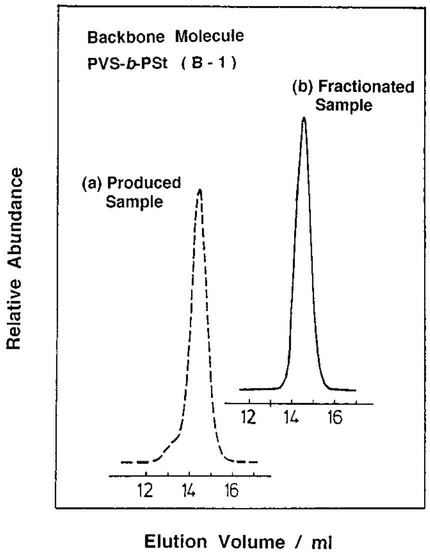

Figure 1. GPC chromatograms of PVS-*b*-PSt block copolymer (B-1) used as a backbone molecule: (a) produced sample without fractionation and (b) fractionated sample using cyclohexane. The experimental conditions are as follows: a carrier solvent of THF, a flow rate of 1 mL/min, an RI detector, and a G5000H6 GPC column.

weight distribution of the resultant backbone was much sharper than that of the initial backbone. The M_w/M_n value of the resultant backbone was determined by GPC measurement using standard polystyrenes. The thus-estimated M_w/M_n value was found to be 1.06. The value of the kinetic average molecular weight, M_k, of the block copolymer, calculated from the amounts of monomer and initiator, coincides with the value of M_n determined by osmometry.

In (2), Is monomer was polymerized for 8 h to yield living polyisoprene carbanions such as PIs^-Cs^+ in the THF/(cumyl)Cs/−78 °C system and PIs^-Li^+ in the Bz/*s*-BuLi/room temperature system. A fraction of these carbanions was terminated by methanol to yield PIs for use as a precursor of the graft. The polymer conversion rates were nearly 100%. Figure 2 shows three GPC chromatograms of the resultant PIs which has a narrow MWD.

In (3), a THF solution of PIs^-Cs^+ was added to the THF solution of PVS-*b*-PSt, or each Bz solution of PIs^-Li^+ for the two grafts was added to each Bz solution of PVS-*b*-PSt. Experimental details of the backbone coupling are described in Table 1. After 24 h, backbone coupling was terminated by pouring a polymerization solution into excess methanol. PIs that did not react with PVS-*b*-PSt was removed from the products of (PVS-*g*-PIs)-*b*-PSt by repeatedly dissolving and precipitating with a mixed solvent of *n*-hexane and *n*-butyl alcohol.

Figure 3 shows three GPC chromatograms of the (PVS-*g*-PIs)-*b*-PSt block−graft copolymer prepared using backbone coupling. Peaks corresponding to M_n values of PIs were not observed in the elution volume; thus, the PIs that did not react with PVS-*b*-PSt was found to be completely removed by fractionation. In order to confirm the absence of contamination of the backbone in the product, a mixture of the backbone and product, namely PVS-*b*-PSt (B-1) and (PVS-*g*-PIs)-*b*-PSt (SGI-2), was tested by GPC measurement. Figure 4 shows the resultant GPC chromatogram, and both original chromatograms are also shown for reference. The mixture exhibits one peak and one shoulder, which are attributed to B-1 and SGI-2, respectively. By comparing this GPC chromatogram with that of Figure 3, the product was found to contain no PVS-*b*-PSt. The other two products of block−graft copolymers (SGI-1 and SGI-3) showed similar GPC behavior.

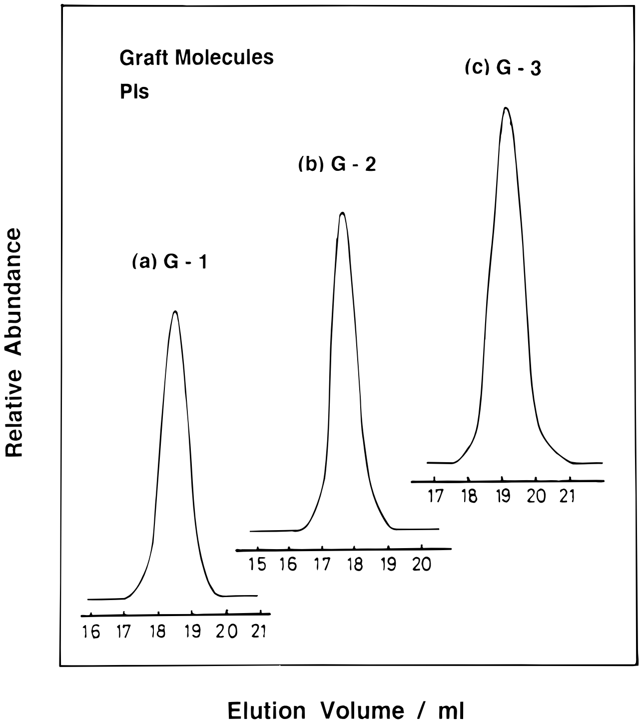

Figure 2. GPC chromatograms of PIs used as graft molecules of (a) G-1, (b) G-2, and (c) G-3 samples. The GPC columns used are G5000H6 for G-1 sample and GMH-6 for the G-2 and G-3 samples.

The sedimentation patterns of the three block−graft copolymers were also examined. As shown in Figure 5, each pattern showed a single sharp peak. Taking into account the results of GPC examination and the sedimentation pattern, the product of each of the three samples was found to contain a (PVS-*g*-PIs)-*b*-PSt block−graft copolymer that had a narrow MWD but no graft and no backbone.

Molecular Characterization. Figure 6 shows the NMR spectra of the block−graft copolymers and the backbone. By comparison of NMR signals of (PVS-*g*-PIs)-*b*-PSt with those of PVS-*b*-PSt, additional NMR signals of block−graft copolymers were found in two regions; 1−2 ppm and 4−6 ppm. These signals are attributed to protons of PIs[25−27] acting as grafts. The molar ratio of the Is unit (grafts content) to a sum of the VS and St units (backbone content) for the block−graft copolymer is estimated from the proton intensities of the corresponding NMR signals in Figure 6. In contrast, the molar ratio of the St unit to the VS unit for the backbone molecule was already estimated from the result of a preparation of the backbone, being described in a footnote to Table 1. Hence, the molar ratio of the Is unit to the St unit for the block−graft copolymers, $(A_{Is}/A_{St})_{NMR}$, is estimated. Thus, the number average molecular weight of a block−graft copolymer, $(M_n{}^{block-graft}{}_{NMR})$, is calculated on the basis of NMR measurements, as follows:

$$M_n{}^{block-graft}{}_{NMR} = M_n{}^{block}{}_{OSM} + M_n{}^{PSt}{}_{OSM}\,(A_{Is}/A_{St})_{NMR}(M_{Is}/M_{St}) \quad (4)$$

where $M_n{}^{block}{}_{OSM}$ and $M_n{}^{PSt}{}_{OSM}$ are respectively the number average molecular weight of the PVS-*b*-PSt block copolymer and that of the PSt segment in the PVS-*b*-PSt block copolymer, as determined by osmometry;

Table 1. Preparation[a] of Three [Poly((4-vinylphenyl)dimethylvinylsilane)-*graft*-polyisoprene]-*block*-polystyrene, (PVS-*g*-PIs)-*b*-PSt, Block−Graft Copolymers

sample code	backbone[b]				grafts				[VS]/[PIs][f]	temp/°C
	code	g	solvent	mL	code	g	solvent	mL		
SGI-1	B-1	1.50	THF	53	G-1[c]	12.5	THF	253	4.4	−78
SGI-2	B-1	0.98	Bz	40	G-2[d]	7.3	Bz	126	4.6	40
SGI-3	B-1	1.12	Bz	43	G-3[e]	3.9	Bz	81	7.9	40

[a] Backbone coupling (grafting onto process) was carried out for 24 h under 10^{-5} mmHg . [b] VS (1.0 g) and St ($32._4$ g) were sequentially polymerized by (cumyl)Cs in THF (580 mL) for 20 min and 1 h, respectively, at −78 °C; the M_k value of $22._9 \times 10^4$, the M_n value of $23._9 \times 10^4$ by osmometry, and the M_w/M_n value of 1.0_6 by GPC. [c] Is ($12._7$ g) was polymerized by (cumyl)Cs in THF (250 mL) for 8 h at −78 °C; the M_k value of $2.1_1\text{x}10^4$, the M_n value of 2.1×10^4, and the M_w/M_n value of 1.0_5. [d] Is ($21._5$ g) was polymerized by *s*-BuLi in Bz (370 mL) for 8 h at room temperature; the M_k value of $1.7_6 \times 10^4$, the M_n value of 1.8×10^4, and the M_w/M_n value of 1.0_6. [e] Is ($11._5$ g) was polymerized by *s*-BuLi in Bz (240 mL) for 8 h at room temperature; the M_k value of $0.31_9 \times 10^4$, the M_n value of 0.32×10^4, and the M_w/M_n value of 1.1_0. [f] Molar ratio of living polyisoprene (grafts molecules) to VS unit (number of possible chemical links).

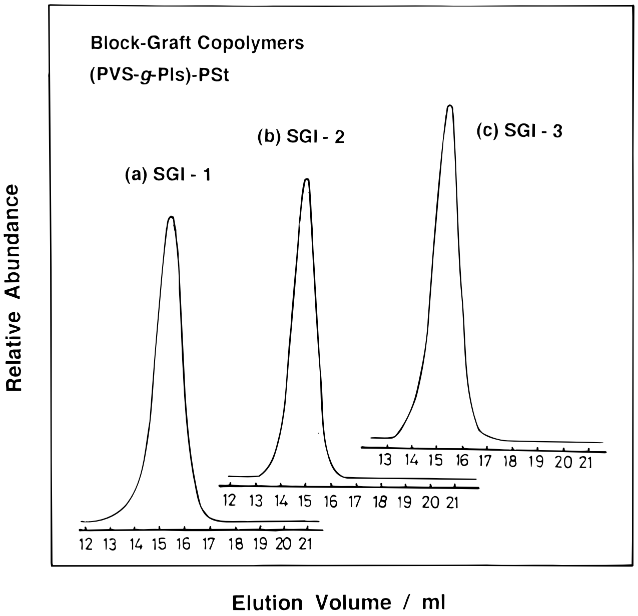

Figure 3. GPC chromatograms of (PVS-*g*-PIs)-*b*-PSt block−graft copolymers of (a) SGI-1, (b) SGI-2, and (c) SGI-3 samples, prepared *via* backbone coupling (grafting onto process). The GPC columns used are G5000H6 for SGI-1 sample and GMH-6 for the SGI-2 and SGI-3 samples.

and M_{Is} and M_{St} are respectively the molecular weights of the Is and St monomers. Furthermore, number average molecular weights of the block−graft copolymers, $M_n{}^{\text{block−graft}}{}_{\text{OSM}}$, were determined by osmometry. As shown in Table 2, the value of $M_n{}^{\text{block−graft}}{}_{\text{OSM}}$ coincides with the value of $M_n{}^{\text{block−graft}}{}_{\text{NMR}}$.

The number of grafts, N^{graft}, per backbone molecule can be defined as

$$N^{\text{graft}} = (M_n{}^{\text{block−graft}}{}_{\text{OSM}} - M_n{}^{\text{block}}{}_{\text{OSM}})/M_n{}^{\text{graft}}{}_{\text{OSM}} \quad (5)$$

When preparing three grafts of PIs, three PIs precursors were obtained for molecular characterization. The M_n values of the three PIs precursors were measured by membrane osmometry and/or vapor pressure osmometry. $M_n{}^{\text{graft}}{}_{\text{OSM}}$ in eq 5 is defined as the resultant M_n value. The thus-estimated N^{graft} values of the three block copolymers are shown in Table 2.

Another essential factor relating to the number of grafts per a backbone molecule is a distribution of the N^{graft} value. As the backbone and graft molecules were linear polymers, their molecular heterogeneity should be estimated from GPC measurements. They had a narrow MWD, as mentioned in a previous section. In contrast, as the block−graft copolymers are star-shaped branched polymers, it is difficult to determine whether the polymers have a narrow MWD or not using only the GPC technique. A principal advantage of the sedimentation measurements would appear to be its independence from GPC measurements. On comparison of the single sharp GPC peak with the single sharp sedimentation peak of each of the three block−graft copolymers, the three block−graft copolymers were expected to have narrow MWD. That is to say, each distribution of the value of $M_n{}^{\text{block}}{}_{\text{OSM}}$, $M_n{}^{\text{graft}}{}_{\text{OSM}}$, and $M_n{}^{\text{block−graft}}{}_{\text{OSM}}$ for the three block−graft copolymers was found to be narrow. Therefore, from eq 5 the distribution of the N^{graft} value for the three samples should be narrow.

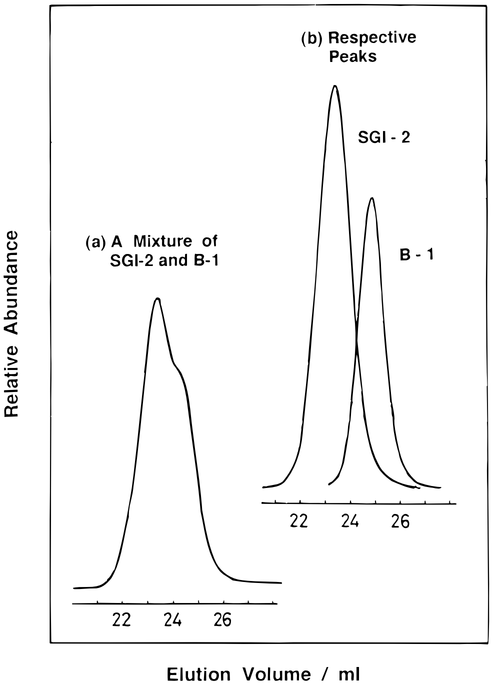

Figure 4. GPC chromatograms of (a) a mixture of a block−graft copolymer (SGI-2) and a backbone molecule (B-1) and (b) a respective sample of the mixture for reference. Two G4000H6 GPC columns were used for measurements.

For the complete characterization of the block−graft copolymer one requires spacing and its distribution of the graft points on the backbone[28] other than those mentioned above. The block−graft copolymers having different spacing or its distribution of graft points are expected to form different conformation and have different physical properties, even though the polymers have the same composition, molecular weight, number, length, and position of grafts. ^{13}C NMR spectroscopy is an absolute method and should provide a graft frequency and distribution of graft points for short chain grafting in polymers such as low-density polyethylene.[29−31] However, the peak intensities in ^{13}C NMR spectra are dependent on the relaxation time of the carbon atoms. This uncertainty in the intensities

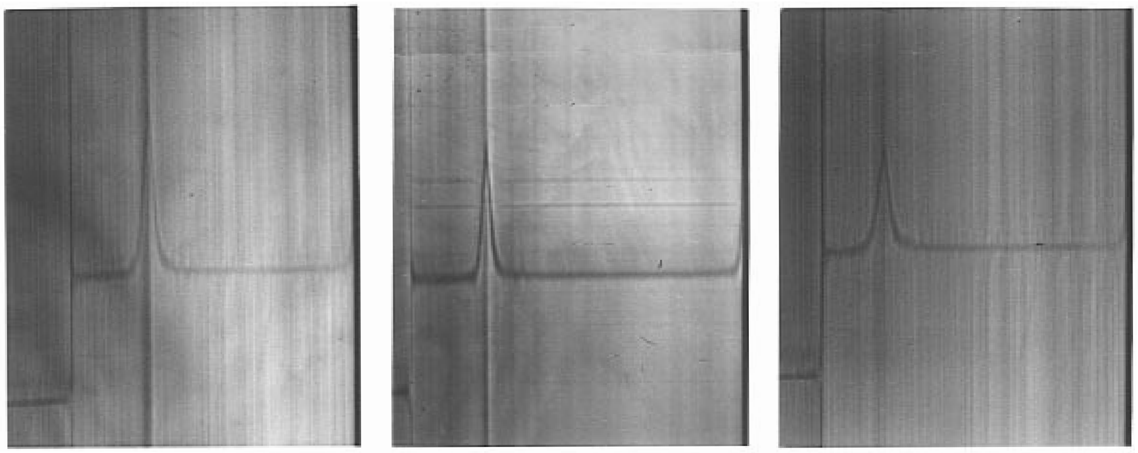

Figure 5. Sedimentation patterns of three (PVS-*g*-PIs)-*b*-PSt block−graft copolymers of (a) SGI-1, (b) SGI-2, and (c) SGI-3: THF solvent, temperature of 25 °C, and a speed of rotation of 59 780 rpm.

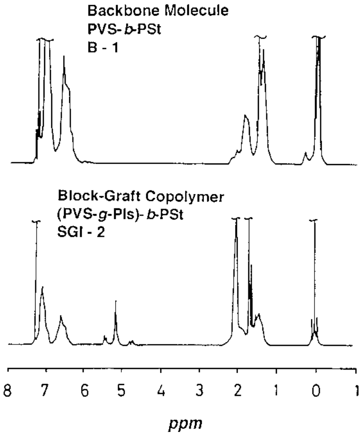

Figure 6. 270 MHz ^{1}H-NMR spectra of a PVS-*b*-PSt block copolymer (B-1) used as a backbone molecule and of a (PVS-*g*-PIs)-*b*-PSt block−graft copolymer (SGI-2).

of the NMR signals of the carbon atoms in different environments results in difficulty in solving the problem of the spacing. Moreover, ^{13}C NMR spectra of long chain grafting in polymers are so complex that the relatively few grafts do not generate sufficient NMR intensities to be clearly separable from configuration and other structural irregularities. Although we have no absolute and reliable method for measuring the spacing and its distribution of graft points for the three block−graft copolymers, special attention should be directed to this essential factor.

The degree of polymerization of PVS in a PVS-*b*-PSt block copolymer is equal to the number of possible chemical links between the backbone and grafts. This characteristic number is termed DP^{VS}. When backbone coupling was performed, the molar quantity of PIs$^-$ carbanions was set at more than 4.4 times larger than that of DP^{VS}. However, the ratio of N^{graft} to DP^{VS} did not approach 100%, but approximately 30%, as shown in Table 2. This result suggests that approximately 30% of the silylvinyl groups of PVS react with living carbanions of PIs$^-$, and the remaining silylvinyl groups are to a large degree sterically hindered[15,21,23,32−34] by grafts. On the other hand, since the reaction of the silylvinyl group of VS with a PIs$^-$ carbanion generates a negative charge in the vicinity of the backbone molecule, the nonquantitative coupling is thought to be due to an electrostatic repulsion between negative charges of the backbone and the PIs$^-$ carbanions. This electrostatic force is given by Coulomb's law and should be inversely proportional to the dielectric constant, ϵ,[35,36] of the solvent used for the coupling reaction. However, the observed result that the $N^{\mathrm{graft}}/DP^{\mathrm{VS}}$ value of SGI-1 prepared in THF (ϵ of 8.20 at 20 °C) is smaller than that of SGI-2 prepared in Bz (ϵ of 2.28 at 20 °C) was found to be contrary to the expected result arising from the electrostatic repulsion. In contrast, the $N^{\mathrm{graft}}/DP^{\mathrm{VS}}$ value was found to increase slightly with decreasing molecular weight of PIs as a graft, on comparison of the $N^{\mathrm{graft}}/DP^{\mathrm{VS}}$ value of SGI-2 with that of SGI-3, even though few results can be considered at the moment. These results suggest that the majority of the nonquantitative coupling[15,21,23,32−34] should be due to not the electrostatic repulsion but steric hindrance.

While a further mechanism of the nonquantitative coupling is not well-known at the moment,[15,21,23] the mutual repulsion between the grafts due to steric hindrance and/or electrostatic repulsion should be uniform, because the backbone and grafts have a narrow MWD. Therefore, the spacing and its distribution of graft points on a PVS block of the backbone appear to be uniform and narrow, respectively. That is, the $N^{\mathrm{graft}}/DP^{\mathrm{VS}}$ value is expected to be attributable to the spacing of graft points.

In conclusion, the steric hindrance and/or electrostatic repulsion results in the preparation of a block−graft copolymer that has a narrow distribution of N^{graft} per backbone molecule and has the uniform spacing and a narrow distribution of graft points: subsequently, the block−graft copolymer has a narrow MWD. In the process of backbone coupling the remaining silylvinyl groups of the PVS block are not able to react with living carbanions of PIs$^-$, after even a long time. The N^{graft} value can be controlled by setting the DP^{VS} value in a PVS-*b*-PSt block copolymer used as the backbone.

Electron Micrographs. Figure 7 shows electron micrographs of three samples of (PVS-*g*-PIs)-*b*-PSt block−graft copolymers cast from a benzene solution. The PIs phase was fixed with OsO_4. The black and white regions in electron micrographs correspond to the PIs phase and PSt/PVS phase, respectively, wherein the PSt/PVS phase is suspected to be a mixed phase of PSt and PVS. No particular attention was directed to the phase structure of PVS in the present study, because the PVS content of each of the three block−graft copolymers is nearly 2 wt %. Conformation, segregation, and microdomain structures of PVS that exist in

Table 2. Molecular Characteristics of Three [Poly((4-vinylphenyl)dimethylvinylsilane)-*graft*-polyisoprene]-*block*-polystyrene, (PVS-*g*-PIs)-*b*-PSt, Block−Graft Copolymers

	backbone			grafts			block-graft copolymer				
	10^{-4} M_n			10^{-4} M_n			10^{-4} $M_n^{\text{block-graft}\ c}$		wt %		
sample code	VS	St	DP$^{\text{VS}\ a}$	Is	N_{graft}	N^{graft}/DP$^{\text{VS}\ b}$	NMR	OSM	VS	St	Is
SGI-1	0.72	23.$_2$	38.$_3$	2.1	10.$_0$	0.26$_1$	44.$_7$	45.$_0$	1.6	51.$_6$	46.$_8$
SGI-2	0.72	23.$_2$	38.$_3$	1.8	10.$_9$	0.28$_4$	44.$_2$	43.$_5$	1.7	53.$_3$	45.$_0$
SGI-3	0.72	23.$_2$	38.$_3$	0.32	12.$_5$	0.3$_2$	28.$_0$	27.$_9$	2.6	83.$_2$	14.$_2$

[a] Degree of polymerization of the VS block in PVS-*b*-PSt block copolymer used as a backbone chain. [b] Ratio of N^{graft} to DP$^{\text{VS}}$. [c] Number average molecular weights of $M_n^{\text{block-graft}}{}_{\text{NMR}}$ determined by NMR measurement, and $M_n^{\text{block-graft}}{}_{\text{OSM}}$ determined by membrane osmometry.

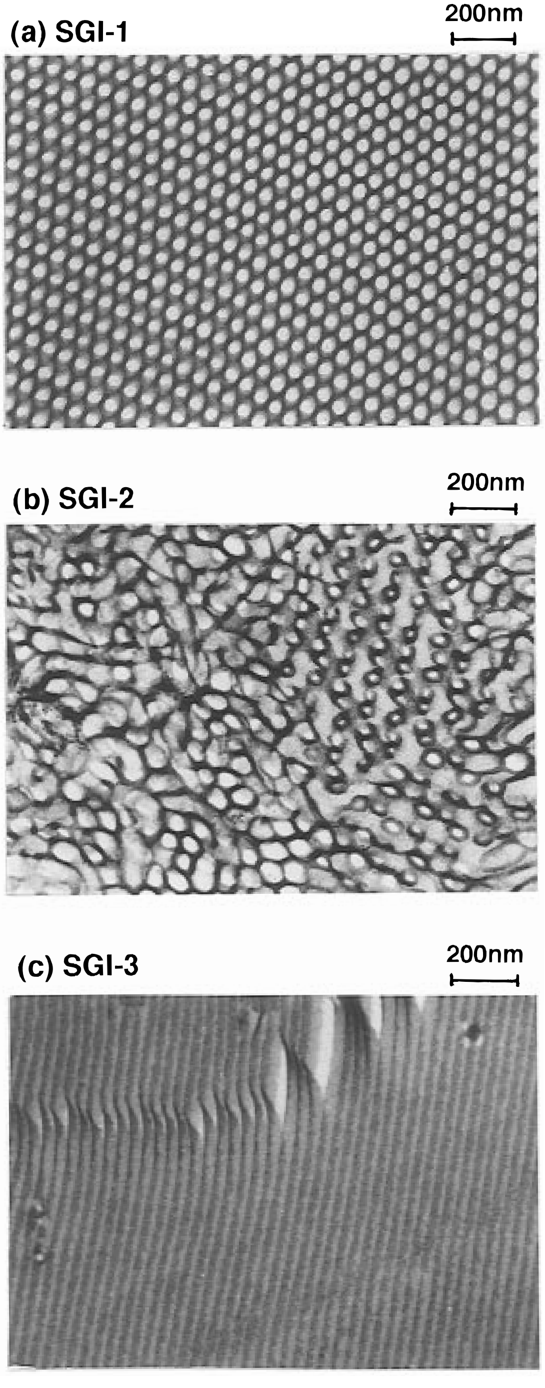

Figure 7. Electron micrographs of block−graft copolymer films of (a) SGI-1, (b) SGI-2, and (c) SGI-3, which were cast from benzene solution and were subsequently stained with OsO_4. White and black regions correspond to PSt/PVS and PIs phases, respectively.

the microphase-separated structure (MS structure) of (PVS-*g*-PIs)-*b*-PSt are important for studying more complex MS structures, such as a star-shaped block copolymer.[37] This subject is going to be studied by other polymer chemists, using small angle neutron scattering[38] of a (PVS-*g*-PIs)-*b*-PSt block−graft copolymer containing deuterated PVS segments. The possible PVS microdomain structure is not discussed at the present stage.

As shown in Figure 7, the three samples formed clear MS structures, which can be observed in all points of the films. Before discussing the morphological behavior of (PVS-*g*-PIs)-*b*-PSt block−graft copolymers, we should comment on the dramatic difference between the MS structure of SGI-1 and SGI-2 which have virtually identical contents of the three monomer compositions and identical molecular weights of three blocks. Anionic polymerization of Is with (cumyl)Cs in THF is known to yield a mixture of geometrical isomers with the vinyl content (1,2-vinyl and 3,4-vinyl units) predominating.[25−27] *s*-BuLi initiation in Bz produces PIs having a high content of 1,4 enchainment (cis-1,4 and trans-1,4 units). Hence, the PIs molecules of SGI-1 and SGI-2 form respectively the geometrical microstructure with the vinyl and 1,4 contents predominating.

From a viewpoint of physical properties of PIs, it has been known that a PIs molecule with high cis-1,4 content has a dipole moment which is aligned in the direction parallel to the chain contour. The PIs exhibits a dielectric relaxation due to fluctuation of the end-to-end distance, which is referred to as the “dielectric normal mode process”.[39,40] According to the dipole−dipole repulsion between the PIs molecules, the end-to-end vectors of the PIs molecule with high cis-1,4 content should be randomly aligned in the solid state so as to minimize a potential energy between the PIs molecules. That is, a regular molecular alignment such as a spherical structure of the block−graft copolymers does not look like a favorable choice for the PIs with high cis-1,4 content. In contrast, a PIs molecule with high vinyl content has been known not to have the dipole moment exhibiting the dielectric normal mode relaxation.[39,40] There should be no additional dipole−dipole repulsion between the PIs molecules with high vinyl content. The dipole effect is capable of determing whether the regular MS structure can be formed or not. A detailed effect of the geometrical isomers on the MS structure of block copolymers having polyisoprene or polybutadiene as a component is not understood at the moment.[41,42] While kinetic effects such as diffusion of a polymer chain[43] may play an important role in MS structure formation, we cannot also explain at the moment how such a difference in the geometrical isomers could result in the difference in the MS structure between SGI-1 and SGI-2.

As a matter of fact, the morphology of the SGI-2 film does not comply with a rule proposed by Molau;[3] namely, the film forms neither globular domains nor a clear continuous phase but a curious amoeba-like domain.[43] The similar morphology of ABC-type three-component block copolymers having a PIs block with high 1,4 content as a component has been reported by Kotaka et al.[43] and Fujimoto et al.[7,8] This result suggests a possibility of controlling the morphology of the block−graft copolymer, to some extent, choosing suitable casting condition.

The SGI-1 film had a PIs content of 47 wt %. A common block copolymer that has one component in an amount of 47 wt % is expected to form a lamellar structure or a cylindrical structure wherein PSt forms a continuous phase surrounding PIs cylinders.[3,4] However, the SGI-1 film showed a spherical structure wherein PIs formed a continuous phase surrounding spheres of PSt/PVS phase. The SGI-3 film contained PIs in the amount of 14 wt %. A common block copolymer that has one component in the amount of 14 wt % is expected to form a spherical structure wherein PSt/PVS forms a continuous phase surrounding PIs spheres. However, the SGI-3 film showed a lamellar structure. That is to say, the morphological behavior of 14% PIs (graft) content of the block−graft copolymer corresponds to that of approximately 50% contents of the common block copolymer, and the morphological behavior of 47% of the block−graft copolymer corresponds to that of approximately 80% of the common block copolymer. From the viewpoint of morphological behavior, the PIs (graft) content dependence of block−graft copolymers was found to shift to the higher PIs content side compared to that of the common block copolymers.

The morphology of block copolymers can be changed by changing the casting solvent.[3,4] This solvent effect is attributed to the solvation power of the solvent for respective blocks. When the concentration of the polymer solution attains a critical concentration,[4,5,37] thereby inducing the formation of the MS structure, the morphology should be determined by the apparent volume fraction of one component containing the solvent. This solvent effect cannot be the dominant factor in the present case, because benzene is a good solvent for each of the PSt, PVS, and PIs blocks. However, the apparent volume fraction is an important factor with regard to the formation of the morphology. The above-mentioned morphological characteristics of the block−graft copolymer suggest that the apparent volume fraction of PIs (grafts) to PVS-*b*-PSt (backbones) at the critical concentration is much larger than the corresponding real volume fraction. One of the causes is thought to be that the graft molecule extends rather than the corresponding unperturbed polymer chain,[6,44,45] because the grafts become crowded[46] in the vicinity of the PVS molecule. Therefore, the block−graft copolymer is believed to form a characteristic MS structure that is distinct from those of common block copolymers.[3,4,6,44] This morphological behavior is a remarkable feature of the model block−graft copolymers prepared in the present study. Further details of the morphological behavior will be discussed elsewhere, including those of other model block−graft copolymers.

Acknowledgment. We are deeply indebted to Prof. H. Hasegawa, Department of Polymer Chemistry, Kyoto University, Kyoto, Japan, for his preparation of the electron micrographs.

References and Notes

(1) Norhay, A.; McGrath, J. E. *Block Copolymers*; Academic Press: New York, 1977.
(2) *Polymer Alloy*; Kotaka, T., Ed.; Tokyo Kagaku Dohjin: Tokyo, 1993.
(3) *Block Copolymers*; Molau, G. E., Aggarwal, S. L., Eds.; Plenum Press: New York, 1970.
(4) Shen, M.; Kawai, H. *AIChE J.* **1978**, *24*, 1.
(5) Hasegawa, H.; Tanaka, H.; Yamasaki, Y.; Hashimoto, T. *Macromolecules* **1987**, *20*, 1651.
(6) Matsushita, Y.; Mori, K.; Saguchi, R.; Nakao, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1990**, *23*, 4313.
(7) Isono, Y.; Tanisugu, H.; Endo, K.; Fujimoto. T.; Hasegawa, H.; Hashimoto, T.; Kawai, H. *Macromolecules* **1983**, *16*, 5.
(8) Matsushita, Y.; Yamada, K.; Hattori, T.; Fujimoto, T.; Sawada, Y.; Nagasawa, M.; Matsui, C. *Macromolecules* **1983**, *16*, 10.
(9) Roovers, J. *Macromolecules* **1987**, *20*, 2300.
(10) Price, C.; Woods, W. *Polymer* **1973**, *14*, 82.
(11) Ito, K.; Usami, N.; Yamashita, Y. *Macromolecules* **1980**, *13*, 216.
(12) Rempp, P.; Franta, E.; Herz, J. *Anionic Polymerization*; McGrath, J. E., Ed.; ACS Symposium Series 166; American Chemical Society: Washington, DC, 1981; p 59.
(13) Rempp, P.; Franta, E. *Pure Appl. Chem.* **1972**, *30*, 229.
(14) Hirano, A.; Takenaka, K.; Yamaguchi, K.; Yamazaki, N.; Nakahama, S. *Polym. Commun.* 1**983**, *24*, 339.
(15) Se, K.; Watanabe, O.; Isono, Y.; Fujimoto, T. *Makromol. Chem., Macromol. Symp.* **1989**, *25*, 249.
(16) Se, K.; Suzuki, M.; Matsuo, T.; Umeda, T.; Ueno, M. *Kobunshi Ronbunshu* (*Jpn. J. Polym. Sci., Technol.*) **1992**, *49*, 817.
(17) Gervasi, J. A.; Gosnell, A. B. *J. Polym. Sci., Part A*: *Polym. Chem.* **1966**, *4*, 1391.
(18) Watanabe, H.; Yoshida, H.; Kotaka, T. *Macromolecules* **1988**, *21*, 2175.
(19) Fujimoto, T.; Nagasawa, M. *Polym. J.* **1975**, *7*, 398.
(20) Se, K.; Kijima, M.; Fujimoto, T. *Polym. J.* **1988**, *20*, 791.
(21) Matsumura, K.; Ueda, K.; Se, K.; Fujimoto, T. *Polym. Prepr. Jpn.* **1984**, *33*, 153.
(22) Se, K.; Matsumura, K.; Kazama, T,; Fujimoto, T. Submitted for publication to *Polym. J.*
(23) Takano, A.; Okada, M.; Nose, T.; Fujimoto, T. *Macromolecules* **1992**, *25*, 3596.
(24) Asami, R.; Oku, J.; Takeuchi, M.; Nakamura, K.; Takaki, M. *Polym. J.* **1988**, *20*, 699.
(25) Bovey, F. *A. High Resolution NMR of Macromolecules*; Academic Press: New York, 1972.
(26) Sato, H.; Ono, A.; Tanaka, Y. *Polymer* **1977**, *18*, 580.
(27) *Kiki Bunnseki no Tebiki*, 2nd ed.; Izumi, N.; Ogawa, K., Katou, S., Shiokawa, J., Shiba, T., Eds.; Kagakudojin: Tokyo, 1996.
(28) Teramachi, S.; Sato, S.; Shimura, H.; Watanabe, S.; Tsukahara, Y. *Macromolecules* **1995**, *28*, 6183.
(29) Koenic, J. L. *Chemical Microstructure of Polymer Chains*; John Willey & Sons: New York, 1980.
(30) Bovey, F. A. *Structural Studies of Macromolecules by Spectroscopic Methods*; Ivin, K. J., Ed.; John Wiley & Sons: London, 1976.
(31) Hsieh, E. T.; Randall, J. C. *Macromolecules* **1982**, *15*, 353.
(32) Roovers, J. E.; Bywater, S. *Macromolecules* **1972**, *5*, 384.
(33) Fujimoto, T.; Tani, S.; Takano, K., Ogawa, M.; Nagasawa, M. *Macromolecules* **1978**, *11*, 673.
(34) Similar phenomena were observed in other block−graft copolymers such as polystyrene-*block*-[poly(hydroxylstyrene)-*graft*-poly(ethylene oxide)]-*block*-polystyrene. The details will be described elsewhere.
(35) Robinson, R. A. *Electrolyte Solutions*; Butterworth & Co., Ltd.: London, 1959.
(36) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*; Reinhold Publishing Corp.: New York, 1959.
(37) Helfand, E.; Wassermann, Z. R. *Macromolecules* **1980**, *13*, 994.
(38) Matsushita, Y.; Nomura, M.; Watanabe, J.; Mogi, Y.; Noda, I.; Imai, M. *Macromolecules* **1995,** *28*, 6007.
(39) Keiichiro, A.; Kotaka, T. *Macromolecules* **1985**, *18*, 466.
(40) Imanishi, Y.; Adachi, K.; Kotaka, T. *J. Chem. Phys.* **1988**, *89*, 7585.
(41) Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Fetters, L. J. *Macromolecules* **1986**, *19*, 2197.
(42) Hasegawa, H.; Tanaka, H.; Yamasaki, K.; Hashimoto, T. *Macromlecules* **1987**, *20*, 1651.
(43) Arai, K.; Kotaka, T.; Kitano, Y.; Yoshimura, K. *Macromolecules* **1980**, *13*, 455, 1670.
(44) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.
(45) Hashimoto, T.; Fujimura, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1660.
(46) Tsukahara, Y.; Ohta, Y.; Seno, K. *Polymer* **1995**, *36*, 3413.

MA961463L