Poly(styrene-*b*-butadiene-*b*-4-vinylpyridine) Three-Block Polymers. Synthesis, Characterization, Morphology, and Mechanical Properties

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ABSTRACT: A *sec*-butyllithium-initiated, sequential block polymerization of styrene (S), butadiene (B), and 4-vinylpyridine (P) in benzene at 10 °C yielded linear three-block polymers which were not heavily contaminated with star-branched components, as revealed by GPC, UV absorption, ultracentrifugation, and osmometry in $CHCl_3$. The solubility of the SBP polymers was tested with more than 30 single solvents, and $CHCl_3$ and *n*-butyraldehyde (BA) were selected as casting solvents. Casting the SBP polymers from $CHCl_3$ and a 9:1 BA/$CHCl_3$ (v/v) mixture gave specimens with two new morphologies, a "ball-in-a-box" and a "three-layer lamellar" structure, respectively. In dynamic viscoelastic behavior, the former showed only two transitions, ascribed to the glass transitions of the polybutadiene and polystyrene phases, while the latter showed three transitions, due to all three phases. In tensile stress–strain behavior, the former underwent a strain-induced "plastic-to-rubber transition" and spontaneous "healing" on subsequent annealing at 60 °C for 14 h, while the latter showed a rather hard, ductile and plastic deformation behavior. The healing of the three-layer-lamellar structure was incomplete after annealing at 60 °C for 14 h.

Introduction

Multicomponent polymer systems[2] often exhibit unique microdomain structures and correspondingly unique physical properties as a result of the microphase separation of the constituent polymers. The morphology of AB and ABA block copolymers such as SBS thermoplastic elastomer has been most extensively studied and found to depend, subject to Molau's rule,[3] on the volume fraction of the phases and, also to some extent, on the conditions of preparation, e.g., the type of casting solvent.[3-6] The morphology–property relationships of these systems have also been studied extensively.[7,8]

Recently studies on ABC three-block polymers have begun to attract much attention. The synthesis of several different three-block polymers have been reported from various laboratories.[9-18] Most of the polymers reported so far are composed of polystyrene (PS) and a polydiene as the A and B blocks, respectively, while the C blocks have consisted of various polymers, including poly(2-vinylpyridine),[9,10] poly(oxyethylene),[11] poly(ethylene sulfide),[12] polyacrylonitrile,[13] poly(α-methylstyrene),[14] poly(p-*tert*-butylstyrene),[15] poly[(4-vinylbenzyl)dimethylamine],[16] and poly(4-vinylpyridine) (P4VP).[17,18] However, their morphological behavior and physical properties are still not clearly understood, presumably because of the complexities of their microdomain structure and also because of the difficulty in distinguishing three phase morphologies. As far as we know, there have been few systematic studies reported on morphologies and properties of ABC three-block polymers.

In a recent communication[17] we reported the synthesis of ABC three-block polymers composed of PS, polybutadiene (PB), and P4VP blocks, which we labeled SBP three-block polymers. Some preliminary results of morphological observations were also presented. In the communication, we reported a new microphase morphology, a "ball-in-a-box" structure. This structure has not been seen before in any other AB-block copolymers or ABC three-block polymers. However, a serious question has been raised as to the quality of such SBP polymers: According to Luxton et al.,[18] an anionic block copolymerization of 4-vinylpyridine (4VP) or 2-vinylpyridine (2-VP) to polystyrene–(polybutadienyl)lithium in toluene has revealed via gel permeation chromatography (GPC) in tetrahydrofuran (THF) carrier that chain linking occurs to yield star-branched materials. Therefore we have repeated a careful molecular characterization study on the SBP three-block polymers. We have ascertained that they have a linear ABC structure with small amounts, if any, of star-branched components. Since the solubility of P4VP is quite different from either that of PS or PB, we expect that an adequate choice of casting solvents might bring about ample possibilities for designing morphologies, through which we might be able to control properties of the SBP three-block polymer specimens. In this article we report details of the studies on the synthesis, molecular characterization, and morphological and mechanical properties of these SBP polymers.

Experimental Section

Polymer Synthesis. The SBP polymers were synthesized by a living anionic polymerization technique under high vacuum (10^{-6} torr). Styrene (ST) and butadiene (BD) monomers were purified by the methods recommended by Fujimoto and Nagasawa.[19] The method involved the following procedures: Distilled benzene was refluxed over potassium benzophenone for a few days until a dark blue color fully developed. The benzene was then placed on a vacuum line, degassed several times, and distilled into a flask containing a sodium mirror and a small amount of anthracene. The solvent was stirred for 1 day and finally distilled into another flask containing *sec*-butyllithium and diphenylethylene for storage. Just prior to use the benzene was distilled directly into a reactor. Freshly distilled styrene was stored with finely ground and degassed CaH_2 and stirred for 1 day with periodic degassing. This procedure was repeated twice. Then the monomer was distilled into a flask containing sodium benzophenone, stirred for a few hours, and distilled into another flask through a U-tube covered with a sodium mirror. The monomer was finally purged for a brief period with *sec*-butyllithium just before collecting in ampules. Butadiene was processed like styrene except that the period of each step was shorter than that for styrene. The 4VP monomer was purified by repeating the procedure of stirring with CaH_2, degassing, and distilling under vacuum four times. Finally the 4VP monomer was distilled into ampules and diluted to 6% (v/v) with the purified benzene.

The polymerization consisted of a three-stage sequential addition of ST, BD, and 4VP in benzene with *sec*-butyllithium as the primary initiator for ST. The concentration was adjusted to keep the final polymer concentration below 3% (v/v) to secure easy and uniform mixing. The reactions were carried out at about 10 °C. At the end of the first and second steps, aliquots were taken to recover the PS precursor and the SB intermediate, respectively, for later characterization. The polymerization of 4VP with polystyrene–(polybutadienyl)lithium ($PS–PB^-Li^+$) posed a difficult problem because of the insolubility of P4VP in benzene (cf. Table I). Upon addition of 4VP monomer into the $PS–PB^-Li^+$

Table I
Solubility of SBP Three-Block Polymers[a]

solvent (δ^b)	SBP-1	SBP-2	SBP-3	SBS[c]
hydrocarbon compounds				
cyclohexane (8.2)	–	0	0	+
benzene (9.1)	0	0	+	+
esters and ethers				
isopropyl acetate (8.6)	–	–	–	0
ethyl acetate (9.1)	–	–	–	–
tetrahydrofuran (9.9)	0	0	0	+
dioxane (10.0)	0	0	0	+
alcohols				
2-ethylhexanol (9.5)	=	=	=	=
isobutyl alcohol (10.7)	=	=	=	=
cyclohexanol (11.4)	0	=	=	–
ethanol (12.7)	=	=	=	=
methanol (14.5)	=	=	=	=
aldehydes				
n-butyraldehyde (9.5)	+	+	0	0
benzaldehyde (10.8)	+	+	+	+
ketones				
2-hexanone (8.6)	–	0	0	+
2-butanone (9.3)	–	–	–	0
cyclohexanone (9.9)	+	+	+	+
halogen compounds				
carbon tetrachloride (8.6)	–	0	0	+
chloroform (9.3)	+	+	+	+
chlorobenzene (9.5)	0	+	+	+
dichloromethane (9.7)	+	+	+	+
1,2-dichloroethane (9.8)	+	+	+	+
1,2,4-trichlorobenzene (~10.5)	+	+	+	+
amines, amides, and nitriles				
butylamine (8.8)	–	–	0	+
n-butyronitrile (10.5)	–	=	=	=
pyridine (10.7)	+	+	+	+
dimethylacetamide (11.1)	0	=	=	–
acetonitrile (11.9)	=	=	=	=
dimethylformamide (12.1)	–	=	=	=
sulfur compounds				
diethyl sulfide (8.8)	–	0	0	+
thiophene (9.8)	0	+	+	+
dimethyl sulfoxide (13.4)	=	=	=	=

[a] 1% (w/v) solutions were tested at room temperature (25 °C). +, clear homogeneous solutions; 0, slightly opaque suspension of micelles; –, heavily opaque suspension of large aggregates; =, slightly swellable or completely insoluble. [b] Solubility parameter values in $(\mathrm{cal\ cm^{-3}})^{1/2}$. [c] SBS sample (Kraton 1101 from Shell Chemical Co.).

solution, the colorless solution rapidly changed to a brick red colored solution of 4-vinylpyridinyl anions. However, as the reaction proceeded and the P4VP composition reached a certain level, the living-anion chains began to form "oil-in-oil" micelles, in which the living P4VP blocks formed the cores and PS–PB blocks the stabilizing arms of the micelles. Since 4VP monomer is a better solvent for P4VP than benzene, the remaining 4VP monomer diffused slowly into the micelle cores, where the polymerization proceeded. Therefore, for SBP-1, for example, the reaction mixture was kept at 10 °C for 72 h under constant stirring. Then methanol was added to terminate the reaction. It took about 5 min for the brick red color to disappear, and a colorless but slightly opaque solution resulted. We prepared three samples, mainly varying in PB-block length. In all three cases the polymer yields were quantitative.

Solubility Test. The solubility of the three SBP samples was tested in over 30 single solvents at room temperature by visual inspection. For the sake of comparison, an SBS sample (Kraton 1101, Shell Chemical Co.) was also used. The results are summarized in Table I. Among these solvents, $CHCl_3$ was a good solvent for all the samples.

Molecular Characterization. The PS and P4VP contents of SB and SBP samples were determined from UV absorbance with a JASCO automatic recording spectrometer (Nihon Bunko Co., Model UNIDEC-5A). The specific absorbance ϵ ($g^{-1}\ cm^2$) was determined for PS and SB samples at 260 nm and for P4VP and SBP samples at 255 nm.

Number-average molecular weights, M_n, of the SB and SBP polymers were determined with a Wescan Instruments recording osmometer (Model 231) in $CHCl_3$ at 28.0 °C. Heterogeneities of the samples were tested by a gel permeation chromatograph (Toyo Soda Ltd., Model HLC-801A) with a triple-detector system, which consisted of a built-in refractometer, a UV-absorption detector (Iatron Instrument Co., Model LC-1), and a low-angle laser light scattering (LALLS) photometer (Toyo Soda Ltd., LS-8) connected in series. A tetrahydrofuran (THF) carrier and commercially available PS elution standards (Toyo Soda Ltd., TSK PS's) were used for determination of M_n and the molecular weight distribution of PS precursors. The GPC run was made with a flow rate of 1.0 mL/min at 30 °C. The polymer concentration was about 0.04% (w/v).

Heterogeneities of SB and SBP samples were tested on the same GPC. The carrier was $CHCl_3$ and the SB and SBP concentrations were 0.12 and 0.15% (w/v), respectively. However, the SBP polymers posed a serious problem due to heavy adsorption onto cross-linked polystyrene gels (Toyo Soda Ltd., TSK gels). For example, in a series of four 2-ft high-resolution, fine-porosity columns [Type G4000H with a permeability limit $M_L = 4 \times 10^5$ for PS and a resolution of 8000 theoretical plates per foot (TPF) for acetone], the SBP polymers were completely adsorbed onto the columns and did not desorb within any reasonable elution time. The columns were replaced by a series of three 2-ft medium-resolution, mixed-gel columns (Type GMH6 with 7000 TPF and a mixture of $M_L = 6 \times 10^5$ and 4×10^8 gels). However, the adsorption effect could not be avoided. Therefore, the heterogeneities of these samples were tested by ultracentrifugation in $CHCl_3$ at 28 °C. A Hitachi analytical ultracentrifuge (Model 1A) equipped with a schlieren optics was employed. The polymer concentrations were 0.25% (w/w). The rotor speed was either 40473 or 55430 rpm. Since $CHCl_3$ has a higher density than the SBP polymers, we observed a floating-boundary pattern instead of a sedimentation-boundary pattern.

Solvent Casting. Usually 0.3–0.5-mm films were cast from 3% (w/v) solutions. The solvents were $CHCl_3$, pyridine, 9:1 benzene/methanol (v/v), and 9:1 *n*-butyraldehyde/$CHCl_3$ (v/v). The solution was cast on a flat-bottomed Teflon cell, and the solvent was allowed to evaporate slowly at room temperature over a period of 7–10 days. The cast film was then dried under vacuum for 3 days at room temperature.

Electron Microscopy. Usually as-cast films or adequately annealed films were trimmed and exposed to a 1% aqueous solution of OsO_4 for 4 days at room temperature. Stained specimens were microtomed to form sections 600-Å thick in the direction normal to the film surface.

The morphological observations of stretched specimens were made as follows: First a specimen was stretched to a given ratio λ. The specimen was attached to a metal block with a flat doughnut shape and exposed to OsO_4 vapor over a 3% aqueous solution for a period of 9 days at room temperature, after which the specimen was removed from the block, trimmed, and further exposed to OsO_4 vapor for 2 more days. The specimen was then microtomed to obtain ultrathin sections that were 400–600-Å thick. The specimen was cut normal to the film surface in the parallel direction (longitudinal) and perpendicular (transverse) to the stretch direction. Morphological observations were also made on SBP specimens which were stretched once to a draw ratio λ, released from tension (they usually did not retract to the original length), and annealed at 60 °C for 14 h. The OsO_4 staining and fixation procedure was the same as that described for the as-cast specimens.

A Hitachi transmission electron microscopy (Model HV-12) was employed at an accelerating voltage of 75 kV.

Mechanical Properties. Measurements of complex tensile moduli E^* were made with a Rheovibron DDV-II (Toyo Baldwin Co.). The frequency was 110 Hz. The temperature was monitored by a copper–constantan thermocouple. The heating rate was about 1 K min^{-1}. Tensile stress–strain behavior was measured on a tensile tester (Iwamoto Seisakusho, Kyoto) at a strain rate of 400% min^{-1} at room temperature (25 °C).

Results and Discussion

Molecular Characterization. Table II summarizes the characteristics of the three series of PS precursors, SB

Table II
Characteristics of the Polymer Samples

code no.	PS precursors obsd[a]		SB intermediates calcd[b]		SB intermediates obsd[c]		SBP three-block polymers calcd[b]		SBP three-block polymers obsd[c]	
	$10^{-3}M_n^S$	$(M_w/M_n)^S$	$10^{-3}M_n^B$	$10^{-3}M_n^{SB}$	$10^{-3}M_n$	$10^{-2}\epsilon_{SB}$	$10^{-3}M_n^P$	$10^{-3}M_n^{SBP}$	$10^{-3}M_n$	$10^{-2}\epsilon_{SBP}$
1	20.2	1.06	22.0	42.2	49	11.16	32.3	74.5	81	67.37
2	23.3	1.04	45.2	68.5	69	7.93	22.3	90.8	93	40.11
3	13.0	1.06	76.7	89.7	96	3.38	22.8	112.5	114	31.28

[a] Determined by GPC with THF carrier at 30 °C. [b] Calculated from M_n^S values and compositions determined from ϵ data by eq 1-3. [c] M_n determined by osmometry in $CHCl_3$ at 28.0 °C; ϵ_{SB} determined by UV absorption at 260 nm, ϵ_{SBP} at 255 nm. For homopolymers, $\epsilon_S = 2330$ at 260 nm and 1960 at 255 nm; $\epsilon_P = 14\,290$ at 255 nm. From these values the compositions (by weight ratio) $y_S{:}y_B{:}y_P$ are calculated as 1:1.09:1.60 for SBP-1, 1:1.94:0.96 for SBP-2, and 1:5.88:1.75 for SBP-3.

intermediates, and SBP three-block polymer samples. A code number was assigned to each series, i.e., S-1, SB-1, and SBP-1. The following simple relations were defined for each series:

$$M_n^{SB} = M_n^S + M_n^B \tag{1a}$$

$$x_J = M_n^J/M_n^{SB} \quad (J = S \text{ or } B) \tag{1b}$$

$$M_n^{SBP} = M_n^S + M_n^B + M_n^P \tag{2a}$$

$$y_K = M_n^K/M_n^{SBP} \quad (K = S, B, \text{ or } P) \tag{2b}$$

Here M_n^S, M_n^B, and M_n^P are the M_n's of the PS, PB, and P4VP blocks in the SBP polymer, respectively. The M_n^S is equivalent to that of the PS precursor and may be directly determined (e.g., by GPC). The M_n^{SB} and M_n^{SBP} are the respective M_n's of the SB and SBP blocks in the samples. On the other hand, x_J is the weight fraction of the J block in the SB intermediate (i.e., $x_S + x_B = 1$), and y_K is that of the K block in the SBP polymer (i.e., $x_S + x_B + x_P = 1$), regardless of whether they are linear chains or branched chains. The relations of the compositions to the M_n^K's are $M_n^S{:}M_n^B = x_S{:}x_B$ and $M_n^S{:}M_n^B{:}M_n^P = y_S{:}y_B{:}y_P$. If the SB intermediate and the SBP three-block polymer have linear AB and ABC structures, M_n^{SB} and M_n^{SBP} should correspond to the osmometrically observed M_n's of the SB and SBP polymers, respectively. If, on the other hand, the SBP polymer has an f-branched $(SBP)_f$ structure, the observed M_n must be f times larger than M_n^{SBP}. If the SBP polymer is a mixture of various f-branched species, M_n is larger than the M_n^{SBP}, according to the relative populations of such species.

Similarly for the specific UV absorbance, ϵ, the following equations hold:

$$\epsilon_{SB} = \epsilon_S M_n^S/M_n^{SB} = \epsilon_S x_S \tag{3a}$$

$$\epsilon_{SBP} = (\epsilon_S M_n^S + \epsilon_P M_n^P)/M_n^{SBP} = \epsilon_S y_S + \epsilon_P y_P \tag{3b}$$

where ϵ_S and ϵ_P are the values of ϵ of PS and P4VP homopolymers, respectively, and ϵ_{SB} and ϵ_{SBP} are those of the SB and SBP samples, respectively. Apparently eq 3a,b are valid regardless of whether the samples are of a linear SBP structure or an f-branched $(SBP)_f$ structure.

Therefore once the values of the ϵ's have been determined experimentally, we can estimate the values of x_J's and y_K's. Then from these values, together with the GPC value of M_n^S, we can readily estimate M_n^B, M_n^P, M_n^{SB}, and M_n^{SBP}. The latter two values may be directly compared with the M_n values determined directly by osmometry in $CHCl_3$. The results are compared in Table II. The reasonably good agreement between the calculated and observed values implies that the SBP polymers have neither highly branched components in large amounts nor a tendency to aggregate in $CHCl_3$. Looking closely at Table II, however, we find a discrepancy between M_n^{SBP} and M_n, especially for SBP-1. This might be partly due to the experimental error involved in the osmometry. However, this might also be due to the presence of star-branched components. If we assume that the weight fraction w_f of an f-branched component is mixed with w_1 $(=1 - w_f)$ of a linear-chain component in the sample, we then have the following relation:

$$M_n^{-1} = w_1/M_n^{SBP} + w_f/fM_n^{SBP} \tag{4}$$

From the data for SBP-1 in Table II, we obtain $w_2 = 0.16$ for $f = 2$, $w_5 = 0.10$ for $f = 5$, $w_{40} = 0.08$ for $f = 40$, and finally $w_\infty = 0.08$ for $f \to \infty$; i.e., if the branched component is exclusively the dimer $(SBP)_2$, the weight percent present is as much as 16%. In other words, assuming the discrepancy between the M_n data is solely due to the presence of branched components, we expect that the amount of such components is less than 16% and more than 8% in the SBP-1 sample.

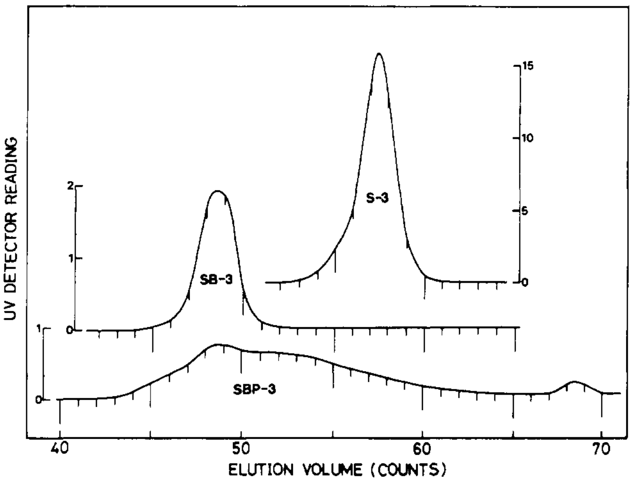


Figure 1. GPC UV chromatograms of the series no. 3 samples, PS precursor S-3, SB intermediate SB-3, and SBP polymer SBP-3, with $CHCl_3$ carrier at 30 °C. The scales in the ordinate are reduced to represent the UV-detector reading for solutions of the same concentration.

Heterogeneities of the SB and SBP samples might also be checked by GPC, using $CHCl_3$ as a carrier. Figure 1 shows a typical set of GPC UV chromatograms of the series no. 3 samples, S-3, SB-3, and SBP-3. The chromatogram of SB-3 implies that it is not contaminated with unreacted S-3 precursor. On the other hand, the chromatogram of SBP-3 badly tails into the higher elution-volume side. However, it is unlikely that branched components are responsible for this retarded elution. Of course, f-branched components, if present, could be eluted after the linear chains having the same molecular weight fM_n^{SBP} but not after the SBP and SB polymers. This retarded elution is rather indicative of a heavy adsorption of the polymer onto

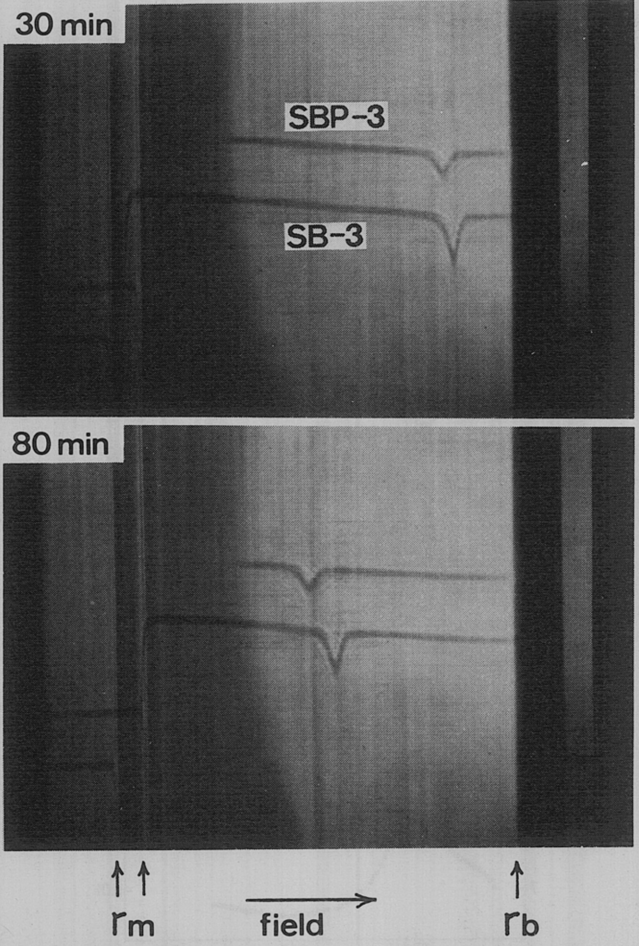
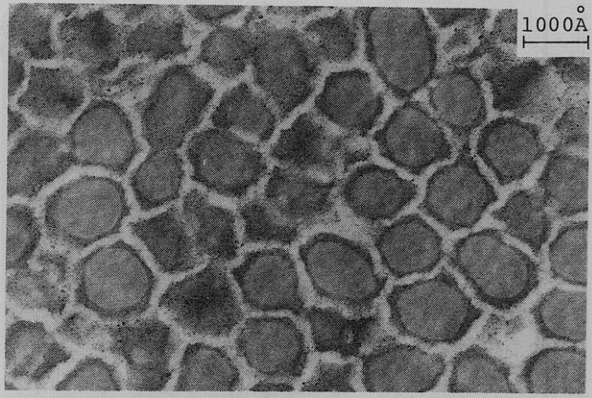


Figure 2. Ultracentrifugal floating patterns of 0.25% (w/w) solutions of SBP-3 (upper pattern) and SB-3 (lower pattern) in $CHCl_3$ at 28 °C centrifuged for 30 (above) and 80 min (below) with 55 430-rpm speed.

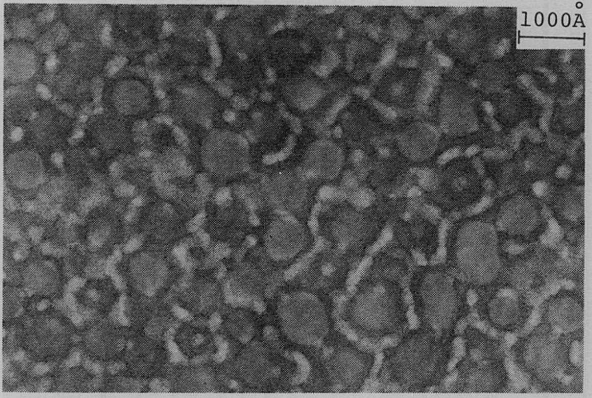
the GPC gels. Also the area under the chromatogram is smaller than that expected from the amount of SBP-3 injected into the GPC. The situation was much worse for other samples which have a larger P4VP content than SBP-3. The performance of GPC with cross-linked polystyrene gels was satisfactory for the PS and SB polymers but not for the SBP polymers.

We have also attempted to examine these polymers by an ultracentrifugation method, using $CHCl_3$ solvent. For each series, solutions of the SB and SBP polymers were placed in a plain-window and a wedge-window cell, respectively, and run simultaneously at the same speed. Figure 2 shows a typical example of schlieren floating-boundary patterns for the SB-3 and SBP-3 samples. After 80-min centrifugation at 55 430 rpm, the SBP-3 boundary clearly separates from the SB-3 boundary, indicating no unreacted SB component. Also the SBP-3 boundary shows neither a rapidly moving-satellite band nor a shoulder, implying that it contains no high molecular weight components such as star-branched materials. The amount of star-branched components, if any, is too small to be detected by the ultracentrifugation method employed here. Similar results were obtained for the other two SBP samples.

As the potential source of the side reactions leading to the branching and cross-linking in the anionic block polymerization of SBP three-block polymers, Luxton et al.[18] referred to the side reactions pointed out by Tardi and Sigwalt,[24] which could occur in an intramolecular manner. We guess that the extent of branching is subject to competitive reactions of $PS–PB^-Li^+$ with the 4VP vinyl group undergoing normal addition, with the pyridine moiety forming the nitranion, and with the P4VP segment attacking the meta position of the pyridine ring or abstracting the α hydrogen.



SBP-1/$CHCl_3$



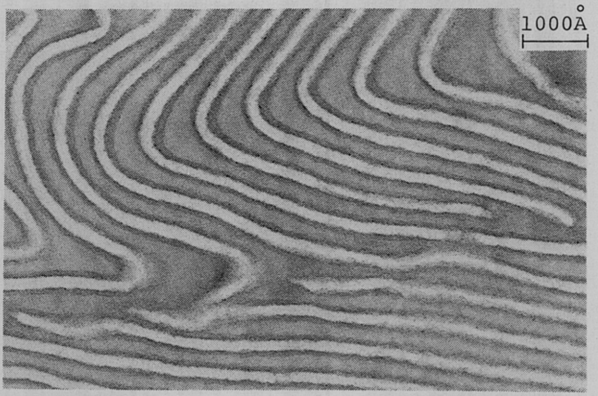
SBP-2/$CHCl_3$

Figure 3. Electron micrographs of SBP-1 and SBP-2 specimens cast from $CHCl_3$ and annealed at 60 °C for 14 h.

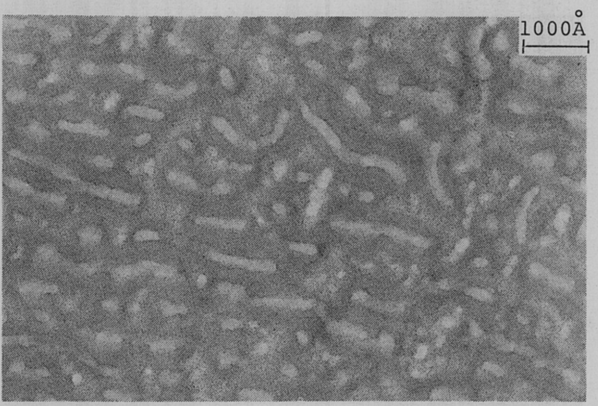
Our block polymerization of 4VP with $PS–PB^-Li^+$ was carried out at 10 °C in benzene and with a ratio of 4VP to $PS–PB^-Li^+$ ends of 200/1 to 300/1, as opposed to Luxton's experiments,[18] which were done at 25–80 °C in toluene with ratios as low as 1/1 to 8/1. All these conditions in our experiments appear to favor the normal addition of 4VP over other side reactions, while those in Luxton's studies encourage side reactions.

Morphological Observations. We examined the morphologies of the SBP specimens cast from several solvents, including $CHCl_3$ and 9:1 *n*-butyraldehyde/chloroform [BA/$CHCl_3$] (v/v) mixture. The latter solvent is unique in the sense that it dissolves the SBP polymers better than SBS-block copolymers.

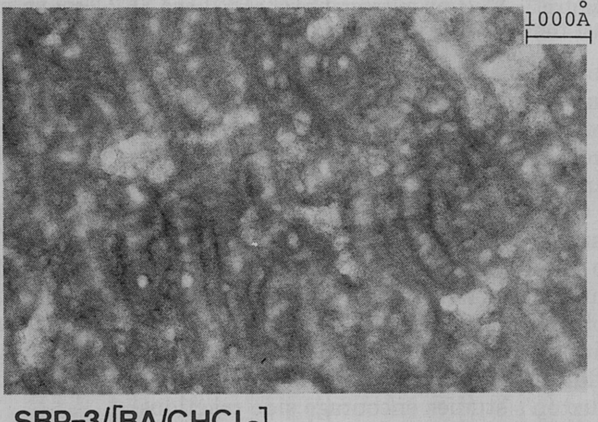
Figure 3 shows electron micrographs of SBP-1 and SBP-2 specimens cast from $CHCl_3$ and annealed at 60 °C for 14 h. The SBP-1 film shows a "ball-in-a-box" morphology, in which gray P4VP spheres have grown somewhat larger during the annealing treatment (cf. Figure 1 in our recent communication[17]). The SBP-2 film shows a morphology similar to that of the as-cast film,[17] but again P4VP spheres have grown larger. A more striking morphology is seen in the BA/$CHCl_3$-cast films shown in Figure 4. Since the solvent dissolves P4VP better than PS or PB, we expected to see continuous P4VP domains. This turned out to be the case. Particularly in the SBP-1 film, we see a "three-layer-lamellar" structure, in which white PS, black PB, and gray P4VP lamellae alternate in the sequence ...SBP·PBS·SBP.... Since two sections per-



SBP-1/[BA/CHCl$_3$]



SBP-2/[BA/CHCl$_3$]



SBP-3/[BA/CHCl$_3$]

Figure 4. Electron micrographs of SBP-1, SBP-2, and SBP-3 as-cast specimens from 9:1 BA/CHCl$_3$ (v/v) mixture.

pendicular to each other as well as to the film surface show identical morphologies, the lamellae are, on the average, parallel to the film surface. Using bulk-density values of 1.05, 0.89, and 1.114 for PS,[25] PB,[25] and P4VP,[20] respectively, we estimated the volume fractions in SBP-1 to be ϕ_S:ϕ_B:ϕ_P = 1:1.28:1.52. The lamellar thickness roughly corresponds to the alternating morphology with these volume fractions. On the other hand, regular morphologies could not be seen in very soft films of SBP-2 and SBP-3 cast from BA/CHCl$_3$.

Dynamic Viscoelastic Properties. Figure 5 shows the temperature dependence of the dynamic Young's moduli *E′*, the loss moduli *E″*, and the tan δ of CHCl$_3$-cast specimens. For all specimens except SBP-3, which was too soft to be subjected to measurement at higher temperature, we observe two *E″* peaks at temperatures of about 200 and 370 K. Presumably these peaks correspond, respectively, to the glass transitions, T_g, of the PB and PS phases.

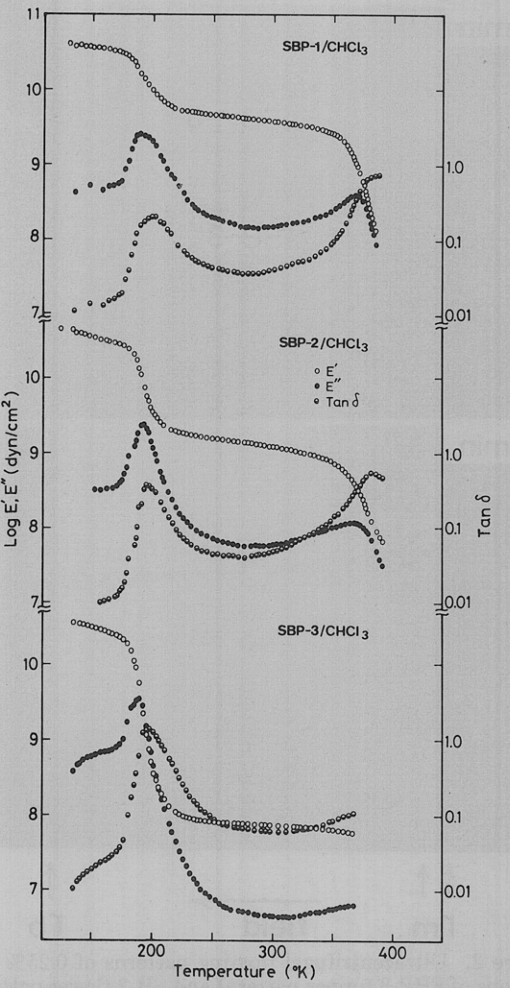


Figure 5. Temperature dependence of *E′*, *E″*, and tan δ at 110 Hz of SBP-1, SBP-2, and SBP-3 as-cast specimens from CHCl$_3$.

Figure 6 shows similar plots for BA/CHCl$_3$ as-cast specimens, for which we observe three transitions. The lowest temperature transition appears around 200 K for all samples. However, other higher temperature transitions differ from one sample to another. For SBP-1, they appear at temperatures of about 370 and 420 K. Frosini and de Petris[20] reported that T_g is 415 K for P4VP and 380 K for P2VP, both prepared by a bulk polymerization at 50 °C, using benzoyl peroxide initiator. Thus the transitions found for SBP-1 presumably correspond to the T_g's of the PB, PS, and P4VP phases. However, for SBP-2 a broad transition appears at temperatures of about 250–300 K, which is followed by a small transition at about 350 K. The transition behavior of SBP-3 is similar to that of the SBP-2 specimen, except that the highest temperature shoulder is much smaller and the drop of *E′* in the PB transition region is much larger in the SBP-3 specimen, indicating that it has a larger PB content than the SBP-2 specimen. (For the composition data, see footnote of Table II.)

Figure 7a shows similar plots for SBP-2 and SBP-3 specimens cast from BA/CHCl$_3$ and then annealed at 60 °C for 14 h. The former showed very peculiar behavior when we carried out a Vibron test under increasing temperature conditions. The highest temperature shoulder around 350 K found in the as-cast specimen was slightly shifted to the higher temperature side. Upon further raising of the temperature, the *E′* and *E″* values began to increase again at about 370 K and a new peak appeared, indicating that a microphase separation had occurred with reorganization of P4VP domains had taken place in this temperature range. On the other hand, we did not find

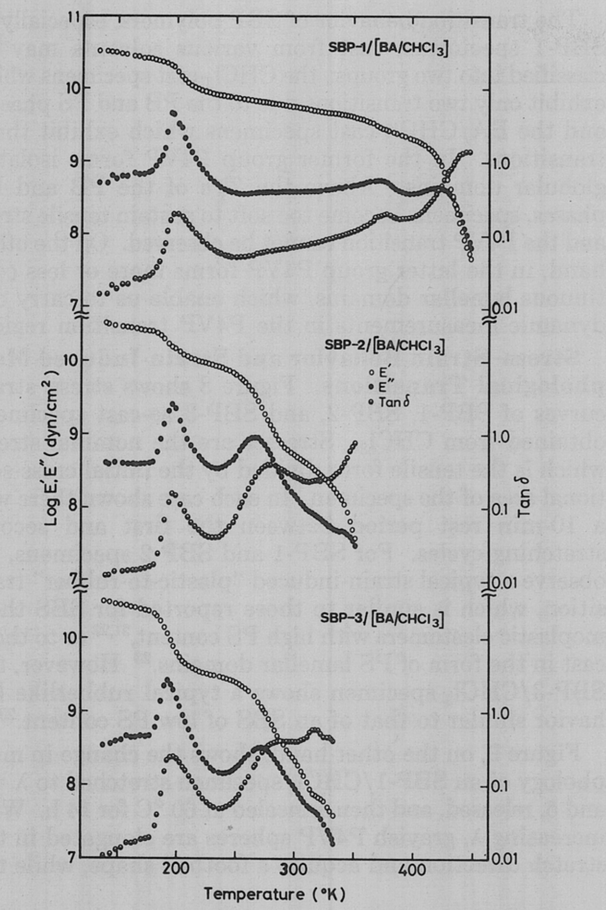


Figure 6. Temperature dependence of E', E'', and tan δ at 110 Hz of SBP-1, SBP-2, and SBP-3 as-cast specimens from 9:1 BA/CHCl$_3$ (v/v) mixture.

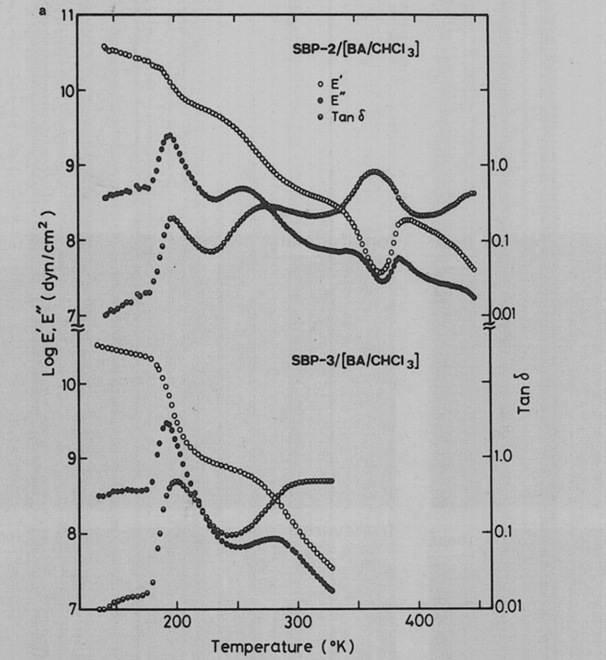
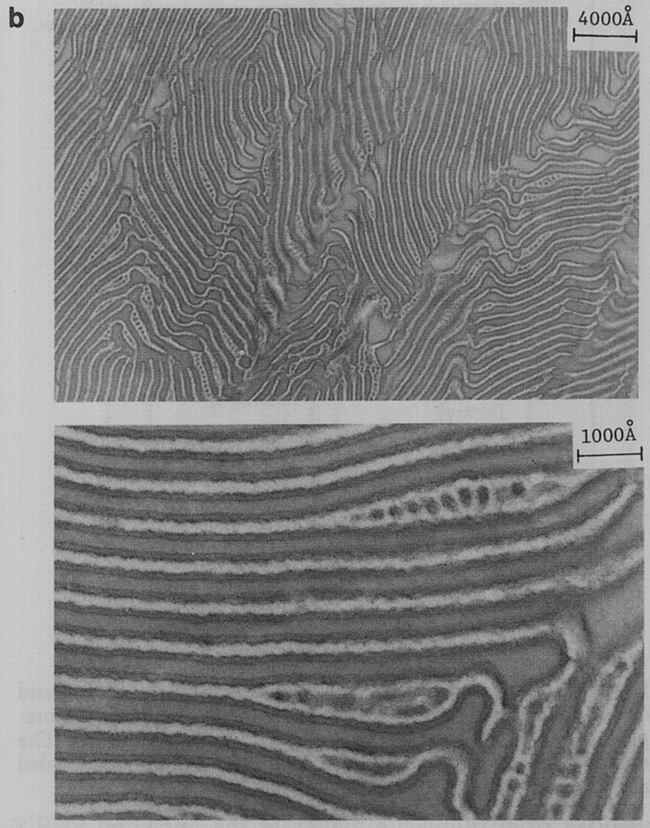
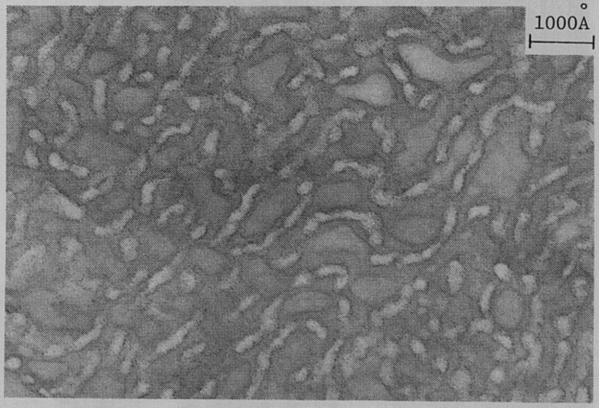


Figure 7a. Temperature dependence of E', E'', and tan δ at 110 Hz of SBP-2 and SBP-3 specimens cast from a 9:1 BA/CHCl$_3$ (v/v) mixture and annealed at 60 °C for 14 h. The measurements were made with increasing temperature.



SBP-1/[BA/CHCl$_3$] after Vibron test up to 450 K



SBP-2/[BA/CHCl$_3$] after Vibron test up to 450 K

Figure 7b. Electron micrographs of SBP-1 and SBP-2 (BA/CHCl$_3$) specimens subjected to the Vibron test up to 450 K (cf. Figure 4).

much influence of annealing on SBP-1/(BA/CHCl$_3$) or SBP-3/(BA/CHCl$_3$) as-cast specimens. In the latter, however, the drop of E' and the peaks of E'' and tan δ became more apparent in the PB transition region, and the highest temperature shoulder almost vanished, implying that the microphase separation of the PB phase had occurred during the annealing treatment at 60 °C.

Figure 7b demonstrates the effects of heating on the morphologies of SBP-1 and SBP-2 specimens to 450 K. The pictures show the morphologies of SBP-1 and SBP-2 (BA/CHCl$_3$) specimens which were annealed at 60 °C for 14 h, heated up to 450 K during the Vibron test, and brought back to room temperature. In the SBP-1 specimen we see a very peculiar "black peas-in-a-pod" structure interspersed among the PS lamellae. We cannot explain at the moment how such microdomains could have resulted. The overall morphology, however, still preserves the three-layer-lamellar structure. On the other hand, in the SBP-2 specimen we see that many irregular-shaped gray domains, presumably of the P4VP phase, have de-

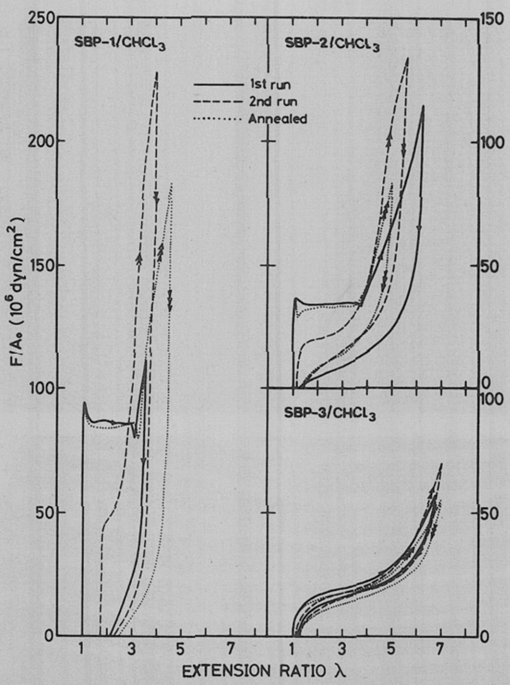


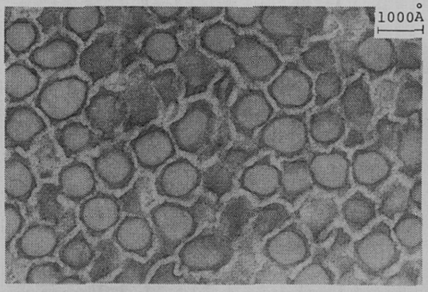
Figure 8. Tensile stress–strain curves of SBP-1, SBP-2, and SBP-3 as-cast specimens from $CHCl_3$ measured at room temperature (about 25 °C) with a 400% min^{-1} extension rate. The curve labeled "annealed" was obtained on the specimen annealed at 60 °C for 14 h after the second run.

veloped from the vague matrix of the unheated SBP-2 specimen (cf. Figure 4, center).

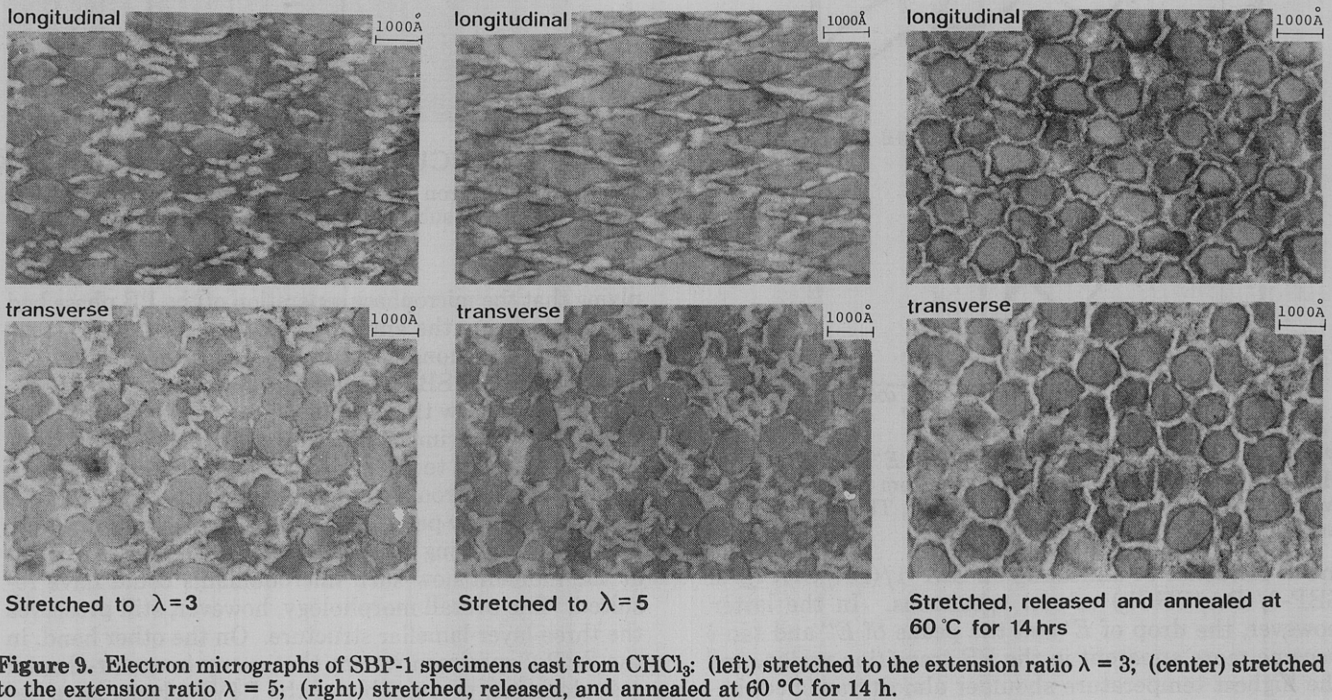
The transition behavior of SBP polymers, especially of SBP-1 specimens, cast from various solvents may be classified into two groups: the $CHCl_3$-cast specimens which exhibit only two transitions due to the PB and PS phases, and the BA/$CHCl_3$-cast specimens which exhibit three transitions. In the former group P4VP forms isolated globular domains. Above the T_g's of the PB and PS phases, specimens become too soft to sustain tensile stress and the P4VP transition cannot be observed. On the other hand, in the latter group P4VP forms more or less continuous lamellar domains, which enable us to carry out dynamic measurements in the P4VP transition region.

Stress–Strain Behavior and Strain-Induced Morphological Transitions. Figure 8 shows stress–strain curves of SBP-1, SBP-2, and SBP-3 as-cast specimens obtained from $CHCl_3$. Stresses are the nominal stress, which is the tensile force divided by the initial cross-sectional area of the specimen. In each case shown there was a 10-min rest period between the first and second stretching cycles. For SBP-1 and SBP-2 specimens, we observe a typical strain-induced "plastic-to-rubber" transition, which is similar to those reported for SBS thermoplastic elastomers with high PS content,[21,22] or to those cast in the form of PS lamellar domains.[23] However, the SBP-3/$CHCl_3$ specimen shows a typical rubberlike behavior similar to that of an SBS of low PS content.[23]

Figure 9, on the other hand, shows the change in morphology of an SBP-1/$CHCl_3$ specimen stretched to λ = 3 and 5, released, and then annealed at 60 °C for 14 h. With increasing λ, grayish P4VP spheres are elongated in the stretch direction and acquire a football shape, while the



SBP-1/CHCl$_3$ as-cast specimen



Stretched to λ=3

Stretched to λ=5

Stretched, released and annealed at 60 °C for 14 hrs

Figure 9. Electron micrographs of SBP-1 specimens cast from $CHCl_3$: (left) stretched to the extension ratio λ = 3; (center) stretched to the extension ratio λ = 5; (right) stretched, released, and annealed at 60 °C for 14 h.

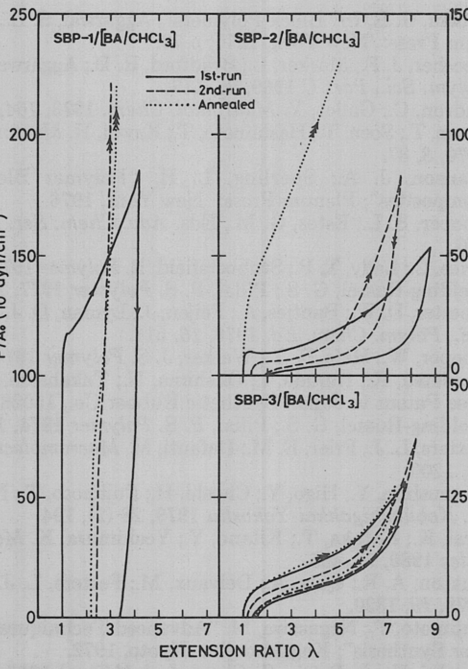


Figure 10. Tensile stress–strain curves of SBP-1, SBP-2, and SBP-3 as-cast specimens from 9:1 BA/CHCl$_3$ (v/v) mixture (cf. Figure 8).

transverse cross sections retain the initial circular shape. The stretched, released, and annealed specimens regain the original morphology of as-cast and annealed films (cf. Figure 3). They also regain the original stress–strain behavior. These specimens possess morphological and mechanical memories. The disrupted domains spontaneously "heal" by annealing under relaxed conditions, as in the case of SBS specimens.[21–23]

Figure 10 compares stress–strain curves of SBP-1, SBP-2, and SBP-3 specimens cast from BA/CHCl$_3$. The SBP-3 specimen shows a soft rubberlike behavior and becomes slightly softened on repetitive subjection to stress, but it recovers its original behavior on subsequent annealing. The SBP-2 as-cast specimen is rather soft but shows a strain-induced plastic-to-rubber transition. However, it becomes hard and somewhat ductile on annealing, as anticipated from the Rheovibron test of the annealed SBP-2 specimen. Finally, the SBP-1 specimen, which has the three-layer-lamellar structure, shows a peculiar behavior. The specimen is rather hard and ductile and somewhat resembles a highly cross-linked elastomer. The behavior is similar to those of compression-molded poly(ST-*b*-BD-*b*-2VP·HCl) specimens.[10] It does not retract on removal of tension. Even after annealing at 60 °C for 14 h, the specimen does not regain its original stress–strain behavior but shows a curve similar to the second run.

The change is also reflected in the morphology shown in Figure 11. After annealing at 60 °C it partly recovers the three-layer-lamellar morphology. At the same time we find that some portions of lamellae are highly distorted and also many tiny crazes and large cracks have developed in the specimen. Healing of the three-layer-lamellar morphology might be better if the annealing were carried out at a temperature closer to the T_g of the P4VP phase.

Conclusion

In our block polymerization in benzene at 10 °C, we were able to prepare linear SBP three-block polymers not heavily contaminated with star-branched materials. The present results on morphological and mechanical studies provide guidelines for the morphological design and the property control of ABC three-block polymers. In this particular system of SBP polymers, we found two new

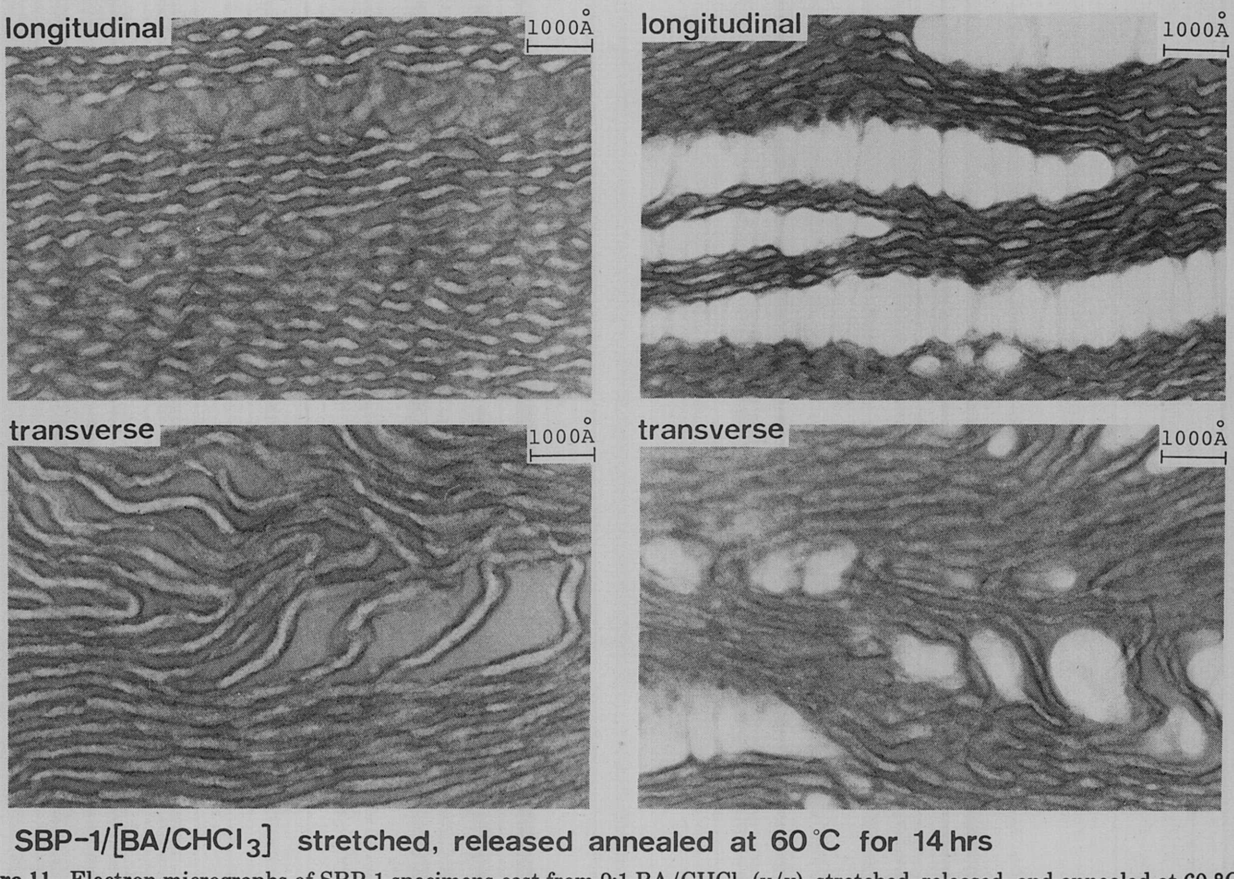


Figure 11. Electron micrographs of SBP-1 specimens cast from 9:1 BA/CHCl$_3$ (v/v), stretched, released, and annealed at 60 °C for 14 h.

regular morphologies. The P4VP phase tends to aggregate in the nonpolar matrix of PS and PB phases. Hence probably the former is the more stable morphology, at least for the SBP-1 sample which has nearly a 1:1:1.5 composition. Only a favorable selective solvent for P4VP such as *n*-butyraldehyde may prevent the aggregation of the P4VP phase into globular domains and may result instead of the formation of continuous lamellar domains. This yields tougher, plastic specimens, while the casting from $CHCl_3$ results in the formation of isolated, globular P4VP domains and yields softer, rubberlike specimens with a substantial healing ability.

A more critical selection of casting conditions such as the use of binary solvent mixtures and the choice of thermal treatment will lead to a finer design of morphology and a more detailed control of mechanical and other properties. We are carrying out such studies on SBP three-block polymers and will report the results later.

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