Morphology control of a poly(styrene-*b*-butadiene-*b*-4-vinylpyridine) ABC three-block polymer by binary solvent casting

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Casting of a poly(styrene-*b*-butadiene-*b*-4-vinylpyridine) ABC three-block polymer from binary solvent systems was carried out to control the microphase-separated structure. Various morphologies including a ball-in-a-box structure and a lamellar structure were observed. On the basis of the change in solvent composition during the casting process, we deduced that the former structure was formed where the selective solvent for poly(4-vinylpyridine) in the binary mixture was lost by vaporization in an early stage of casting. On the contrary, the latter structure was formed under a casting condition when solvents were equally distributed into the three phases and/or the distribution and the composition of solvents had not varied significantly during the casting process. If casting proceeds from an opaque solution in which some aggregates already exist, or if the selective solvent for one or two of the three block segments vaporizes faster than other solvent in an early stage of casting, the morphology becomes a random and indefinite structure.

Keywords ABC-type block polymer; poly(styrene-*b*-butadiene-*b*-4-vinylpyridine); vinylpyridine-containing block polymer; morphology; binary solvent casting; microdomain structure; viscoelastic property

INTRODUCTION

A number of authors, notably Merrett[1], Aggarwal[2] and others[3-5], have attempted to control the physical properties of graft and block copolymers by controlling the morphology of specimens. Morphological studies revealed that one of the constituent polymers which was soluble in the casting solvent usually constituted a continuous phase and the other polymer formed isolated domains. When another solvent which dissolved the other polymer was used, the inverse phase structure emerged and different physical properties appeared[1].

Recently several ABC-type three-block polymers were prepared to study microphase separation and other properties[6-18]. Some authors[15,16] reported that the morphological behaviour of ABC three-block polymers (and their homopolymer blends[16]) could be explained successfully by expanding Molau's rule for AB and ABA type block copolymers[19]. However, the general rule governing the morphological behaviour has not been found for many other ternary block polymers. This situation is presumably due to complexity and diversity of their micro-domain structures.

In previous publications[17,18] on poly(styrene-*b*-butadiene-*b*-4-vinylpyridine) three-block polymers (SBP), we described new definite morphologies which we called 'ball-in-a-box' and 'three-layer lamellar' structures. Furthermore, systematic studies on the morphological property of SBPs with different composition and molecular weight revealed that these definite structures were found only in SBP specimens having not only equal block composition but also rather low molecular weight. However, in our previous research, we did not extensively explore the possibility of controlling the morphology by adjusting the method of specimen preparation such as casting solvent and moulding temperature.

In this study, we attempted to apply the method of selective solvent casting[1-5] to control the morphology of solvent-cast films of an SBP sample. To this purpose, it was necessary to cast the polymer from a solvent which was good, at least for one or two block segments. However, any single selective solvents usually did not dissolve the SBP sample as a whole[18]. Therefore, for casting SBP we used several mixed binary solvents which gave a transparent solution to obtain films having controlled morphology. A problem in using a binary solvent mixture as a casting solvent was that, as the casting proceeded, the solvent composition eventually changed owing to difference in volatility of the constituent solvents. Therefore, we first examined the change in solvent composition during casting for several binary systems. To achieve a satisfactory casing of SBP, the polymer, first of all, must be soluble and should not form visibly large aggregates in the casting solvent. We em-

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ployed a post-polymerization method and examined the morphology of the aggregates in a post-polymerized specimen of dilute solution of the SBP polymer, using 2-hydroxyethyl methacrylate (HEMA) and/or methyl methacrylate (MMA) as one of the components of the casting solvent.

We discuss here a method of controlling morphologies and the process of their structure formation during the casting of an SBP sample from a variety of binary solvent systems.

EXPERIMENTAL

Polymer sample

Details of the method of synthesis and characterization of SBP samples were reported previously[18]. In brief, the three-block polymers were synthesized by stepwise anionic polymerization of styrene, butadiene and 4-vinylpyridine in benzene using *sec*-butyllithium as the primary initiator for styrene. The sample used in this study was SBP-1 having number-average molecular weights of polystyrene (PS), polybutadiene (PB) and poly(4-vinylpyridine) (P4VP) equal to 20 200, 22 000 and 32 300, respectively[18].

Recently, Ishizu *et al.*[20] commented on the basis of gel permeation chromatogram (g.p.c.) in our previous publication[18] that P4VP block of our SBP polymers might have a heterogeneous molecular weight distribution. These authors have misunderstood the g.p.c. pattern but also ignored the results orf of sedimentation velocity analysis and other evidence given in the literature[18] to prove the purity of the SBP polymers. The number-average molecular weight M_n of the SBP polymers determined directly from osmometry in $CHCl_3$ coincided with those calculated from the M_n values of the S and SB precursors and the composition of the SB and SBP polymers[18]. This evidence also rules out the possibility that the SBP polymers might be contaminated either with low molecular weight homopolymers or with highly branched, high molecular weight contaminants. Although we do not repeat the details of the characterization study[18] here, we emphasize that the SBP polymer used in this study has a linear and well defined ABC architecture with narrow distributions of each blocks.

Solubility test

The solubility of the SBP sample was tested for eight mixed binary solvents. For each binary solvent system, the test was carried out as follows. First, the polymer was dispersed in one of the binary solvents (3% (w/v) conc.). Then the other component was added slowly. The solubility was decided by visual inspection at room temperature. The solvents used were tetrahydrofuran (THF), benzene (BZ), methyl ethyl ketone (MEK), cyclohexane (CYH), ethanol (EtOH), nitromethane (NTM), methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA). All the solvents were commercially available (extra-pure grade), and used without further purification except MMA and HEMA. These polymerizable solvents were washed with alkali and water several times, and vacuum distilled to remove inhibitor just prior to use.

Post-polymerization method

Freshly distilled MMA and a small amount of benzoyl peroxide (Wako Chemical Co., extra-pure grade) were introduced in a ampoule containing 30 mg of SBP-1 under nitrogen atmosphere. The polymer was dispersed using an ultrasonic vibrator (the mixture was opaque). Then the correct amount of freshly distilled HEMA was introduced and shaken gently to make a homogeneous solution. The ampoule was sealed after degassing by a freeze–thaw method. The polymer concentration was 3% (w/v), and monomer mixtures of different volume ratios were prepared. The ampoule was kept in a water bath at 15°–18°C. Then the polymer mixture was allowed to polymerize by exposing to u.v. light for about two days. The polymerized bulk specimen was then taken out by breaking the glass ampoule carefully.

Solvent casting

Films were cast from 3% (w/v) solutions. The binary solvents examined were THF/X (4/1 v/v) with X being methanol (MeOH), ethanol (EtOH) and n-propyl alcohol (PrOH), Y/EtOH (4/1 v/v) with Y being CYH, MEK and BZ, and MMA/MeOH (4/1 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

As-cast films of usually 0.3 to 0.5 mm thickness and post-polymerized specimens were trimmed and exposed to a 1% aqueous solution of OsO_4 for 4 days at room temperature. Stained specimens were microtomed to sections 40 nm thick in the direction normal to the film surface. A Hitachi transmission electron microscope (Model HV-12) was employed. The accelerating voltage was 75 kV.

Mechanical property

Measurements of complex tensile moduli E^* were made with a Rheovibron DDV-II (Toyo Baldwin Co.). The frequency was 110 Hz. The heating rate was about $1 K min^{-1}$.

Analysis of casting solvent mixture

The composition of binary solvent under casting was determined by gas chromatography. Solvent systems examined were the same as those in the solvent casting experiments. A gas chromatograph (Shimadzu Model 4BM) equipped with a hydrogen flame ionization detector was employed. A polyethylene glycol coated column of 3 m length (Shimadzu, 25% PEG on Chromosome WAW (80/100)) was used with N_2 carrier at flow rate of $40 ml min^{-1}$. For THF/X and Y/EtOH systems, the column temperature was set at 68°C and 70°C, respectively. For the MMA/HEMA system, a temperature elevation technique was employed. The range of temperature was from 100° to 150°C. The rate of temperature elevation was $10°C min^{-1}$.

The sampling procedure was as follows. A 4 ml aliquot of 2.5% (w/v) polymer solution of SBP-1 was prepared in a small flask with a cover glass. Then the solvent was allowed to evaporate very slowly for about 5 days to complete the casting) by adjusting the cover glass. While the solution was being condensed, a 5 to 10 mg aliquot of the polymer solution was sampled at proper intervals. The aliquot was immediately diluted by 1 ml of 1,2-dichloroethane, and 3 to 4 μl of the diluted sample was injected to the gas chromatograph to determine solvent composition (wt%). These data were plotted against polymer concentration (wt %) which was determined from both the initial polymer weight and the solution weight at each sampling time correcting the sampling loss.

RESULTS AND DISCUSSION

Solubility test for mixed binary solvents

Among the solvents used, MeOH, EtOH, NTM and HEMA are good solvents for P4VP (S^P), and BZ and MMA are good solvents for both PS and PB (S^{SB}). THF also dissolves PS and PB (S^{SB}), but is good for PS more than for PB. MEK is a selective solvent only for PS (S^S), and CYH for PB (S^B). We made the following combinations of binary solvents, S^{SB}/S^P, S^S/S^P and S^B/S^P.

Figure 1 shows schematically the solubility of SBP-1 in binary solvents. THF/EtOH, BZ/EtOH, THF/NTM and MMA/HEMA dissolved SBP-1 to give a transparent solution, at least in a certain range of composition. On the other hand, the solutions in MEK/EtOH, CYH/EtOH, MEK/NTM and BZ/NTM were opaque in any composition and never became transparent. In the former group, three distinct regions I, II and III could be found (see THF/EtOH system). In the opaque regions, there were large aggregates of SBP-1 which scattered visible light.

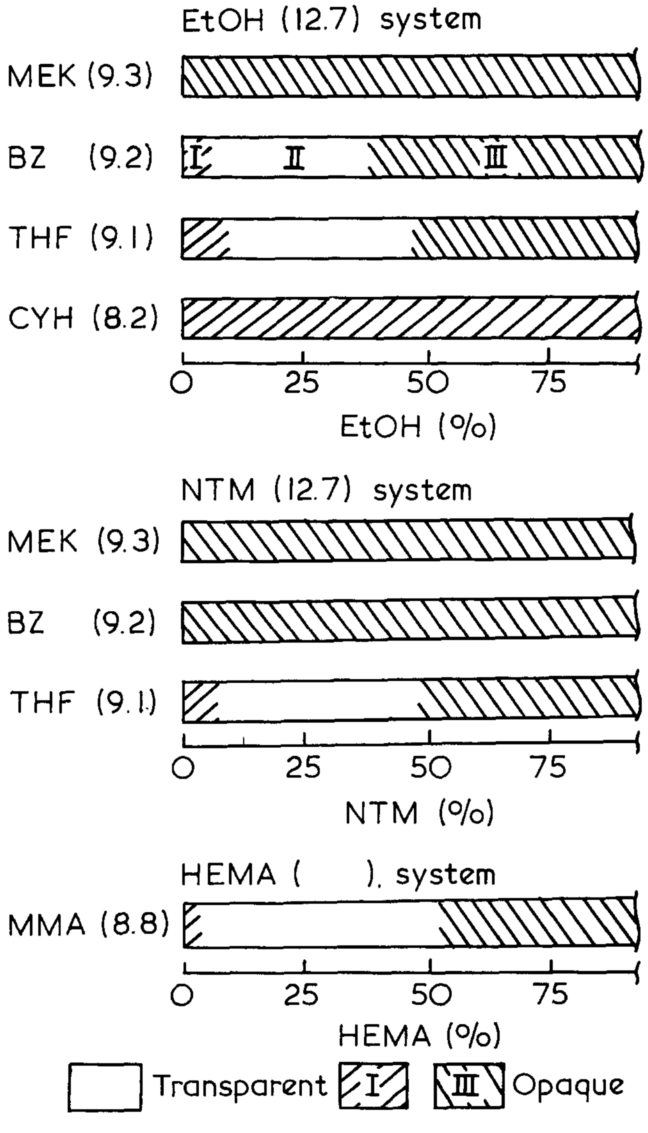


Figure 1 Solubility of SBP-1 for mixed binary solvents

We selected MMA/HEMA solution of SBP-1 as a typical model to confirm the structure of SBP aggregates in a binary solvent system. The solvent monomers were post-polymerized[21] by u.v. irradiation to fix the structure of polymer aggregates in the poly(methyl methacrylate) (PMMA)/poly(2-hydroxyethyl methacrylate) (PHEMA) matrix. *Figure 2* shows transmission electron micrographs of post-polymerized specimen, SBP-1/(PMMA/PHEMA), with 9/1 and 3/1 PMMA/PHEMA ratio. The polymer concentration was 3% (w/v). In the opaque region I (9/1 ratio), worm-like micelles of about 1 μm length are observed, and small micelles are also seen dispersed in the PMMA/PHEMA matrix. Presumably, since these large micelles scattered visible light, the initial solution and also the post-polymerized specimen looked opaque.

Besides the opaque region, *Figure 2b* shows the structure of SBP-1 in the transparent region II. The SBP-1 forms rather small aggregates (<200 nm diameter) which are too small to scatter visible light. The non-existence of a clear boundary of the aggregates shows that all the three block segments are dissolved in the solvent in this composition.

Morphologies and mechanical properties of as-cast films

THF/alcohol system. We chose a series of THF/alcohol (4/1) binary solvent systems, in which the alcohol was either MeOH, EtOH or PrOH, and cast SBP-1 from these mixtures. Since these solutions of SBP-1 were all transparent, there were no large multimolecular micelles in the initial solutions of about 3% (w/v) polymer concentration. For these mixtures, the boiling point and vapour pressure of THF and alcohols are different from one another. Therefore, as casting proceeds, the solvent composition might change, becoming either THF-rich or alcohol-rich. This composition change will bring about different structures of polymer micelles in concentrated solution and finally a variety of film morphologies. Boiling point and vapour pressure at 25°C of solvents used are listed in *Table 1*.

Figure 3 shows electron micrographs of SBP-1 cast from THF/alcohol (4/1). The structures are entirely different from one another. Especially, in THF/MeOH film, a lamellar structure is observed. However, looking closely at the micrograph, we notice that PB phase does not form perfect lamellae but discontinuous domains. The morphology of SBP-1 cast from THF/EtOH is highly

Table 1 The boiling point (b.p.) and vapour pressure ($P_{25°C}$) of solvents for binary system*

Solvent	b.p. (°C)	$P_{25°C}$ (mmHg)
THF	66.0	197
MeOH	64.7	125
EtOH	78.3	60
PrOH	97.2	20.9
MMA	100.3	38
CYH	80.7	98
MEK	79.6	90.6
BZ	80.1	95.2

* Riddik, J. A. and Burger, W. B., 'Organic Solvents', Wiley Intersceince, New York, 1970

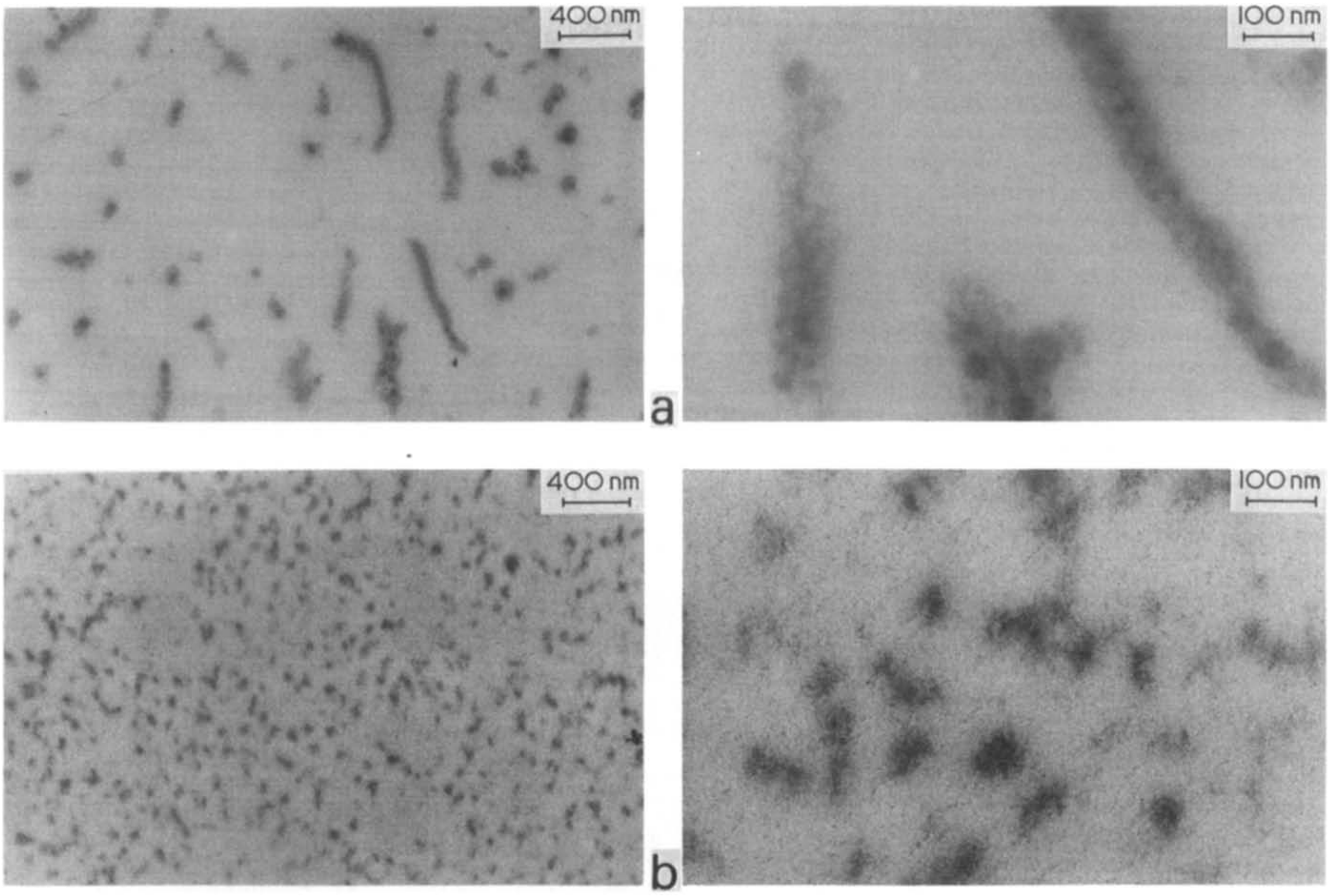
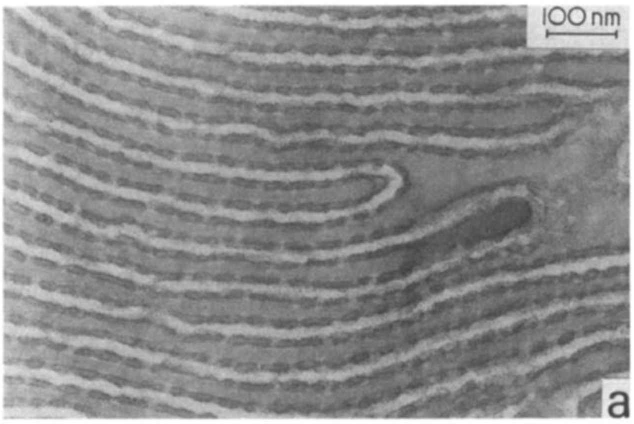


Figure 2 Electron micrographs of SBP-1/(PMMA/PHEMA) post-polymerized from 3% (w/v) solution. The ratio of PMMA/PHEMA is (a) 9/1 and (b) 3/1

irregular. In the specimen, we see irregular worm-like domains of PS and PB dispersed randomly in P4VP phase. On the other hand, in THF/PrOH cast film, a definite structure is not observed and each phase cannot be distinguished clearly. The result suggests that definite morphology such as a lamellar structure can hardly be achieved if the casting proceeds from a binary solvent consisting of two components with widely different volatility and solvent power.

Figure 4 shows temperature dependence of dynamic mechanical property of the same specimens. In all curves, we observed three glass transition temperatures at 190,



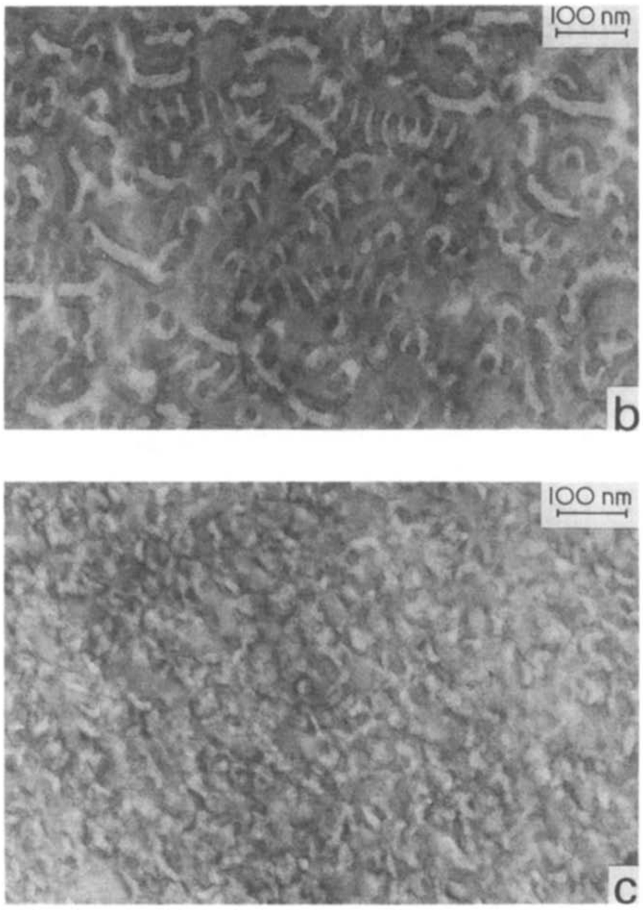


Figure 3 Electron micrographs of SBP-1 as-cast specimens from THF/alcohol (4/1) mixtures. The alcohol is (a) MeOH, (b) EtOH and (c) PrOH

370 and 430K related to the T_g of PB, PS and P4VP phases[22], respectively. This result suggests that the P4VP domain forms a continuous phase in all three specimens. The values of dynamic storage modulus $E'(400)$ at 400K can be related to the degree of phase continuity of P4VP domains, as far as the segment composition is equal. For example, the $E'(400)$ of SBP-1 specimen having a ball-in-a-box structure was too small (probably of the order of 10^5 N m^{-2}) to be detected by the Rheovibron tester[18]. On the contrary, for a three-layer lamellar structure[18,23], the $E'(400)$ becomes as high as 2.0×10^8 N m^{-2}. The P4VP lamellar phase sustains the test specimen not to flow even at high temperature. The value of $E'(400)$ of SBP cast from THF/alcohol are 4.0×10^7, 1.5×10^8 and 1.1×10^8 N m^{-2} for THF/MeOH, THF/EtOH and THF/PrOH cast films, respectively. Among these films, THF/EtOH cast film has the highest value of $E'(400)$. This result suggests that this film has more continuous P4VP domain than the other two specimens.

Other binary solvent systems. For THF/alcohol systems, we attempted to control the morphology of SBP by utilizing the difference in solvent volatility. In this subsection, we describe the results of other binary solvent systems, Y/EtOH (4/1) (Y being CYH, MEK or BZ). These solvents had nearly the same boiling point (see *Table 1*), but had different solubility towards each block segment of SBP. CYH/EtOH and MEK/EtOH were both a good solvent for two of the three block segments; the former dissolved PB and P4VP, and the latter dissolved PS and P4VP preferentially. Therefore, the initial casting solutions were not transparent, and large multimolecular micelles might exist in the mixtures. On the other hand, BZ/EtOH was a good solvent for all three block segments and the solution was transparent. We observed morphologies of cast films of these systems.

Figure 5 shows electron micrographs of SBP-1 cast from these binary solvents. In CYH/EtOH cast film, PS, PB and P4VP phases are randomly entangled with one another to form a three-dimensional network. The struc-

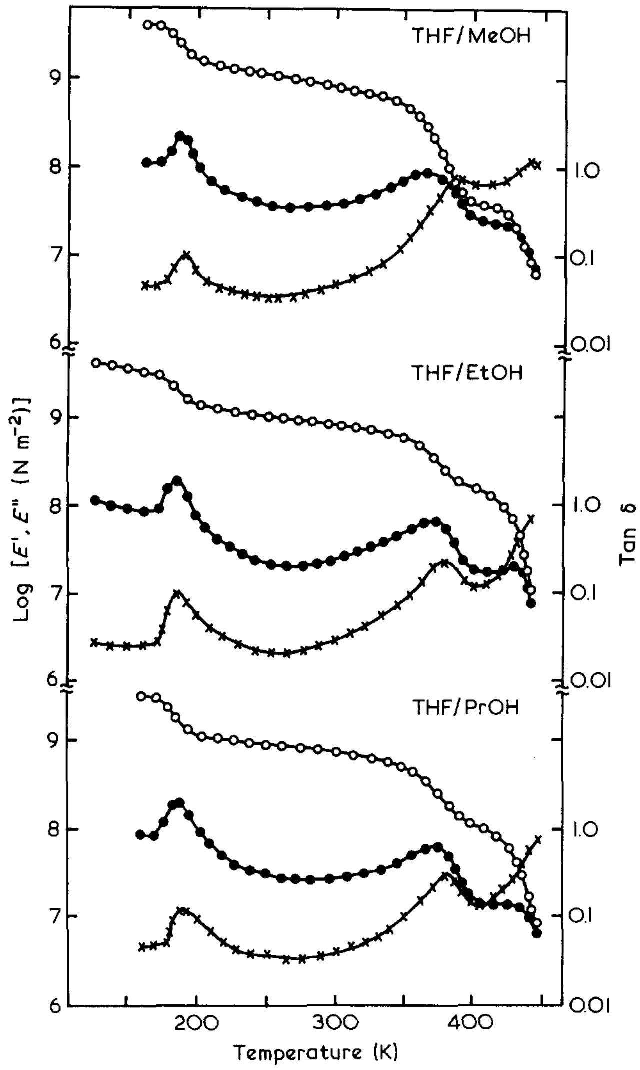


Figure 4 Temperature dependence of E' (○), E'' (●) and tan δ (X) at 110 Hz of SBP-1 as-cast specimens from THF/alcohol (4/1) mixtures. The alcohol is MeOH, EtOH and PrOH as shown

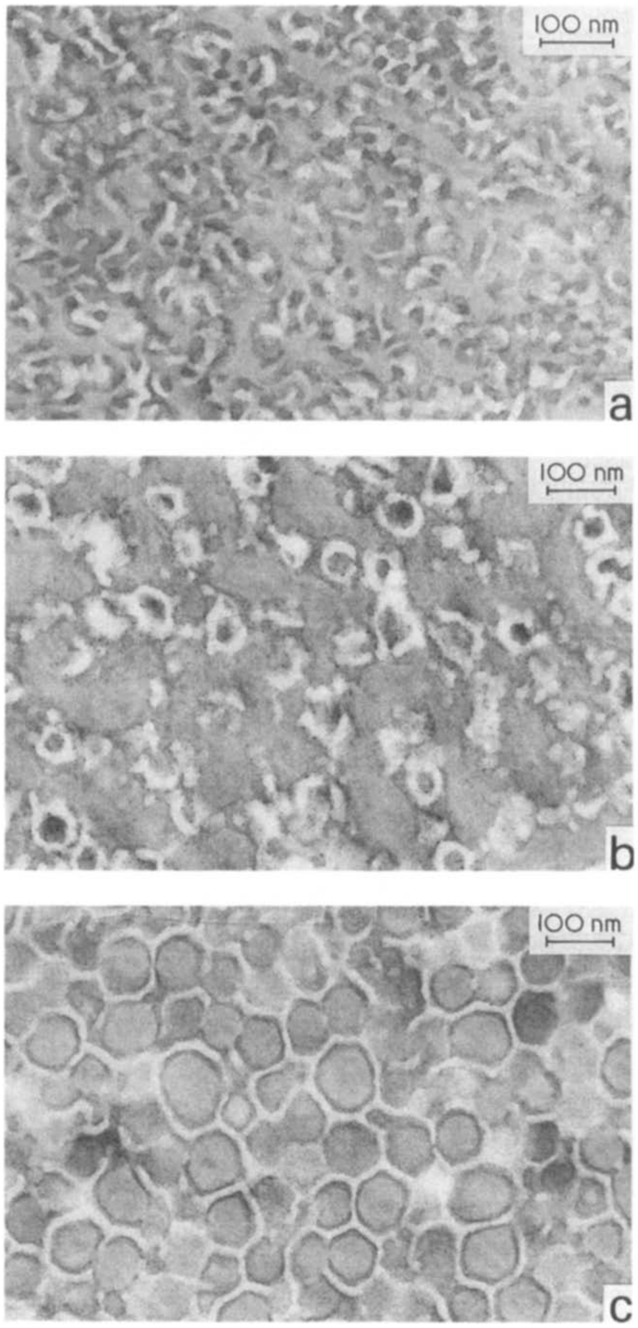


Figure 5 Electron micrographs of SBP-1 as-cast specimens from Y/EtOH (4/1) mixtures. Y is (a) CYH, (b) MEK and (c) BZ

ture is very much similar to the morphology of the THF/EtOH cast film. In MEK/EtOH cast film, we observed curious ring-shaped PS domains dispersed randomly in PB and P4VP domains of ambiguous shapes. Definite morphologies such as lamellar and ball-in-a-box structure were not observed in these specimens. On the other hand, in BZ/EtOH cast film, the observed morphology is a ball-in-a-box structure, in which P4VP globular domains are contained in honeycomb type PS cells and PB fills the gap[17,18].

One puzzling result we obtained is that the size of these P4VP globules is 2 to 3 times larger than that expected from the M_n of the P4VP blocks. A few possibilities may conceivably explain this result. One possibility is that the SBP polymer might contain some low molecular weight homo-P4VP impurities, which are entrapped in the P4VP globules. Another possibility is that some SBP polymers themselves might be entrapped in the globules. The third possibility is that the P4VP blocks might assume an extended conformation in the globules.

The first possibility may be ruled out, because our characterization study[18] indicated that the SBP polymer is fairly pure. Also it is rather unlikely that the product of a sequential anionic living polymerization of S, B and 4VP could be contaminated with homo-P4VP rather than the PS and SB precursors. Secondly, small molecular weight homopolymer contaminants should reduce the M_n of the smaple. This was not the case in the SBP polymer[18]. On the other hand, the second possibility is more likely to be the case. In our previous study[18], we detected the presence of PB component entrapped in PS domains of an SBP-1 specimen cast from P4VP selective solvent such as butyraldehyde and later annealed at 450K. There is a possibility that, in the specimen cast from PS- and PB-selective solvent, the P4VP domains may contain some entrapped SBP polymers. As to the third possibility, we have at present no evidence either to rule out or to confirm it.

Temperature dependence of dynamic mechanical property of these cast films are shown in *Figure 6*. For CYH/EtOH cast film, three glass transitions related to PS, PB and P4VP domains are observed, and the mechanical behaviour is quite similar to that of THF/EtOH cast specimen. This result corresponds to the morphological similarity between the two specimens. For MEK/EtOH specimen, on the contrary, the E' value at ambient temperature is rather small. This small E' is presumably due to the isolated ring-shaped structure of PS domains. Moreover, temperature dependence of the moduli is unusual for this specimen, i.e. the E'' peak appears as a doublet in each of the glass transition regions of PB, PS and P4VP. This result indicates that six different phases must exist in MEK/EtOH cast specimens. However, they are, if they exist, too complicated to be distinguished from one another in the micrograph. For BZ/EtOH cast films, dynamic mechanical behaviour is similar to that observed in $CHCl_3$ cast films having a ball-in-a-box structure[18]. The glass transition of the P4VP phase cannot be detected by dynamic mechanical spectroscopy. However, the existence of three T_g's was clearly demonstrated by differential scanning calorimetry for those ball-in-a-box specimens[24].

From these results, we deduce that the film morphology becomes an indefinite random structure when the polymer is cast from an opaque solution in binary solvents even with the same boiling point.

Change of solvent composition during casting

Figure 7 shows changes of polymer concentration and solvent composition during the casting from THF/alcohol (4/1) systems. In the figure, the ordinate represents SBP-1 concentration and the abscissa ROH content in the solvent. As the casting proceeds, the ROH content changes along the arrows in each system. In THF/EtOH and THF/PrOH systems, the solvent composition tends to alcohol-rich side during the whole stage of casting. That is, THF vaporizes much faster than the other two alcohols due to their different volatility (cf. *Table 1*). Therefore, the solvent for PS and PB block segments, especially good for PS, becomes a minor component and the selective solvent for P4VP a major component during the casting.

On the other hand, in THF/MeOH systems, slightly higher volatility of MeOH than that of THF makes the solvent composition THF-rich in the early stage of casting ($<10\%$ conc. of SBP-1). However, in the subsequent stage of casting, the THF content begins to decrease and converges gradually to a constant value of about 80%.

Figure 8 shows changes of polymer concentration and solvent composition during the casting from Y/EtOH (4/1) (Y being CYH, MEK or BZ) systems. The boiling

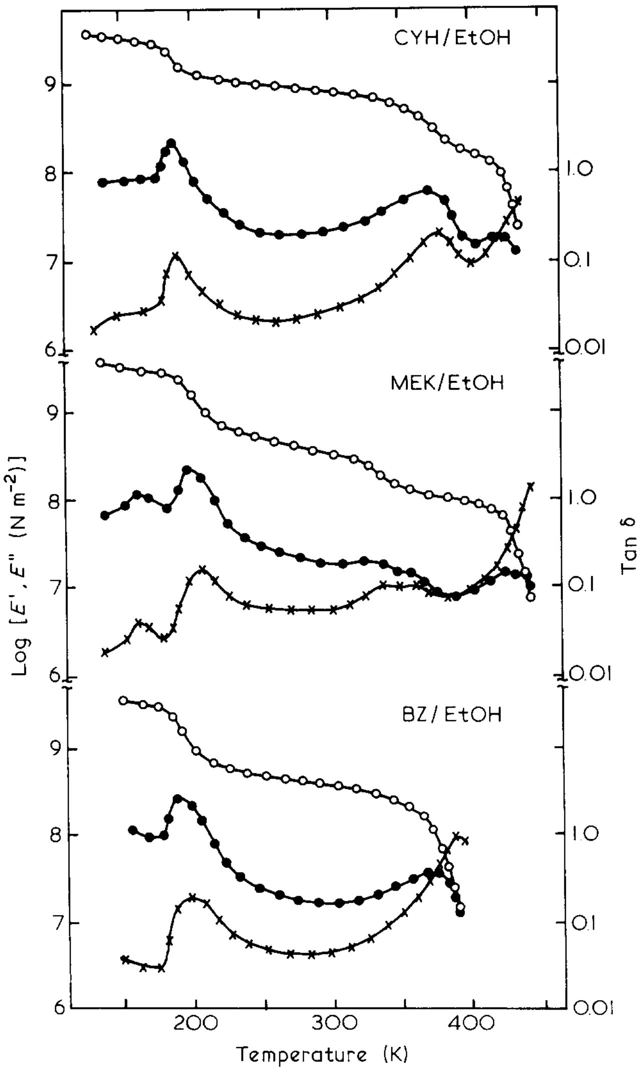


Figure 6 Temperature dependence of E' (○), E'' (●) and tan δ (X) at 110 Hz of SBP-1 as-cast specimens from Y/EtOH (4/1) mixtures. Y is CYH, MEK and BZ as shown

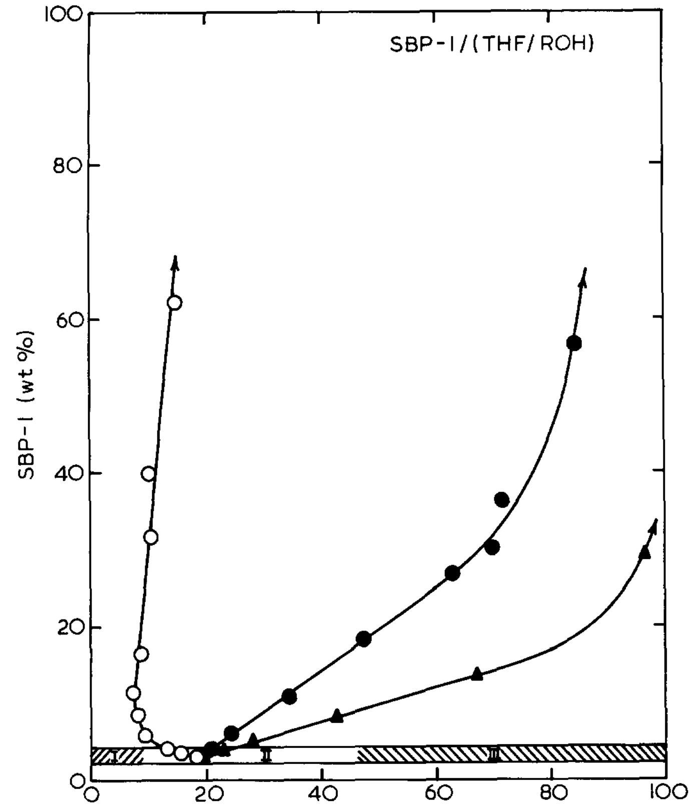


Figure 7 Changes of SBP-1 concentration and solvent composition casting from THF/alcohol (4/1) mixtures. The alcohol is MeOH (○), EtOH (●) and PrOH (▲)

points of CYH, MEK, BZ and EtOH are nearly equal to one another (see *Table 1*). However, some difference are observed among the casting behaviour. In CYH/EtOH and BZ/EtOH systems, EtOH rapidly evaporates and the composition curves are similar to each other beyond the 30% polymer concentration, where the EtOH content is virtually zero. On the other hand, in MEK/EtOH system, the EtOH content increases gradually to 50% composition at about 50% polymer concentration.

Morphology control of SBP. The phase separation behaviour of AB and ABA block copolymers in a selective solvent for either one of the A or B segments was described as an isothermal phase diagram (structure as a function of the concentration) by Sadron *et al.*[21] The diagram was divided into three regions which emerge as the polymer concentration increases. However, as a matter of fact, the microphase-separated structure developed in concentrated solution would often be fixed at a certain concentration level and results in the morphology in the solid state. Therefore, the final morphology may be influenced by two factors; one is arising in an early stage of casting in dilute solution of several per cent polymer concentration, and the other is in the region where the polymer concentration is sufficiently high and the structure is about to be fixed.

A point characteristic of the ball-in-a-box structure formation is presumably that P4VP segments first coagulate to form core domains in an early stage of casting. If this assumption is correct, a ball-in-a-box structure will be formed whenever aggregates of P4VP segments exist in the solution in an early stage of casting. We investigated the morphology and the solvent composition of SBP-1/(MMA/MeOH (4/1)) as a typical example. An electron micrograph of a cast specimen and the solvent composition curve during the casting are shown in *Figure 9*. As the boiling point of MMA is much higher than that of MeOH, the solvent composition quickly reaches 100% MMA at only about 5% polymer concentration. The morphology looks like a ball-in-a-box structure. The dynamic mechanical behaviour was also very similar to that of BZ/EtOH and ChCl$_3$ cast films[18], and T_g of P4VP phase was not detected. However, looking closely at the micrograph, we notice that the PS domain does not wrap PB and P4VP phases perfectly, and some P4VP globular domains are linked together. We suspect this is not a true ball-in-a-box structure as observed in BZ/EtOH and CHCl$_3$ cast specimens. Presumably, rather slow coagulation of P4VP segment is necessary to form a definite ball-in-a-box structure.

On the other hand, in THF/MeOH system, the solvent composition stayed almost always within the region corresponding to the transparent region in the early stage of casting. Therefore, unlike in BZ/EtOH system, aggregates of P4VP segments may not exist. The constant ratio SP/SSB ($\sim$1/5) even in the region of higher polymer concentration suggests that the volume fraction of each domain swollen with the solvents is nearly equal in this region. That is, the lamellar structure may be thermodynamically more stable than any other morphologies according to theories of microphase separation[25,26].

In THF/EtOH and THF/PrOH systems, the initial casting solutions were transparent. However, a great difference exists between these systems and THF/MeOH or BZ/EtOH systems. In the latter systems, only one block segment coagulates (or presumably not) in the early stage

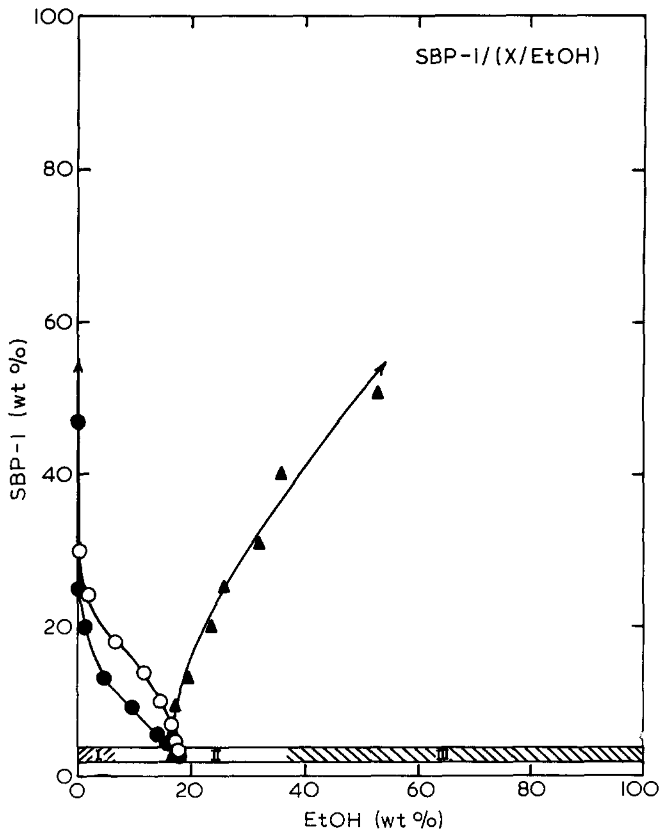


Figure 8 Changes of SBP-1 concentration and solvent composition casting from Y/EtOH (4/1) mixtures. Y is CYH (○), BZ (●) and MEK (▲)

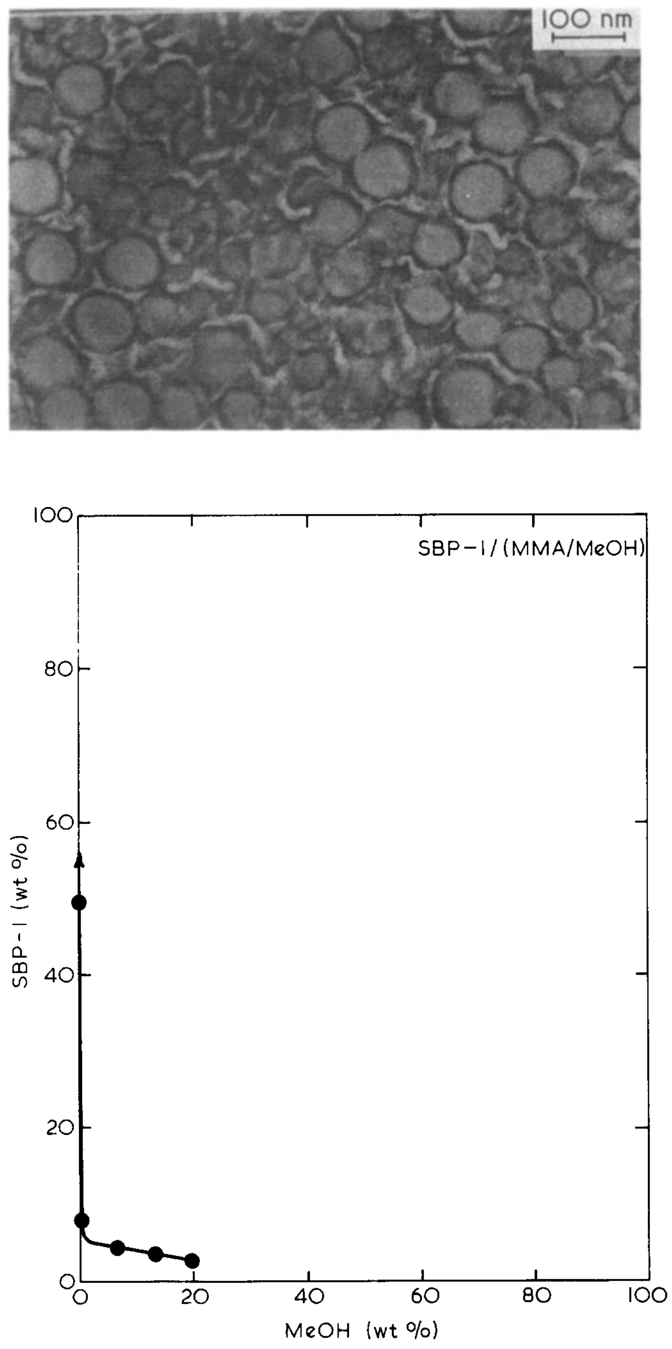


Figure 9 An electron micrograph of SBP-1 as-cast specimen from MMA/MeOH (4/1), and change of the polymer concentration and solvent composition during the casting

of casting. In contrast, in the former system, because the solvent composition tends to be alcohol-rich even in the early stage of casting, both PS and PB segments must begin to coagulate to form multimolecular micelles in the P4VP solution phase. That is to say, an indefinite structure presumably arises in the rather high concentrated region when two of the three block segments simultaneously aggregate to make multimolecular micelles. Especially in the THF/PrOH system, the decrease in THF content was more rapid than that in the THF/TtOH system. This tendency presumably causes the indefinite and random morphology observed in the THF/PrOH cast film.

Comparing CYH/EtOH and MEK/EtOH systems to THF/MeOH and BZ/EtOH systems, we notice that the initial solutions of casting are opaque in the former, but transparent in the latter. Large multimolecular micelles exist in the opaque solution. In these opaque systems, as the solvent composition tends to be CYH-rich or EtOH-rich during the casting, a second block segment may further aggregate. That is to say, two of the three block segments precipitate to form multimolecular micelles.

From the above discussions, we may conclude that the casting conditions necessary to form definite morphologies in SBP-1 specimens are as follows. First, multimolecular micelles should not exist in the initial solution of casting, that is, the casting solution should be transparent. Secondly, at least more than one block segment must not aggregate in an early stage of casting. In our experiments, as the solubility parameters of PS and PB are not so far apart, preferential solvents for both PS and PB segments (common solvents) such as BZ and THF may be easily obtained. On the other hand, there are few preferential solvents for both PS and P4VP or both PB and P4VP. Therefore, to find a casting condition under which gradual aggregation of only PS or PB segment occurs during the casting is almost impossible for usual binary solvent systems.

Casting of SBP-1 from various mixed binary solvents revealed several different morphologies including a lamellar and a ball-in-a-box structure. On the basis of solvent composition change during casting, we deduced the process of microphase-separated structure formation. The lamellar structure may be formed under a peculiar casting condition such that the solvents are equally distributed into the three phases, and the distribution and the solvent composition remain nearly the same all through the casting process. On the contrary, the ball-in-a-box structure may be formed when the P4VP selective solvent is lost by vaporization in the early stage of casting.

If casting proceeds from an opaque solution, or if selective solvents for two of the three block segments vaporize much faster than the other solvent in the early stage of casting, the morphology will become a random and in definite structure.

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