

Synthesis and morphological studies of polyisoprene-*block*-polystyrene-*block*-poly(vinyl methyl ether) triblock terpolymer

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Dedicated to Professor Imanishi on the occasion of his retirement

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Abstract

The triblock terpolymer (PI-*b*-PS-*b*-PVME) consisting of polyisoprene (PI), polystyrene (PS) and poly(vinyl methyl ether) (PVME) was synthesized by coupling reaction between living PI-*b*-PS anion and end-chlorinated PVME prepared via living cationic polymerization. This polymer is an amphiphilic block polymer and unique in a sense that it exhibits complex phase behavior because PS and PVME have a lower critical solution temperature (LCST)-type phase diagram while PI and PS (or PVME) have an UCST-type phase diagram. This unique architecture would result in a step-wise microphase separation to form a three-phase microdomain structure. It was observed by transmission electron microscopy with ultrathin sections that the toluene-cast film of PI-*b*-PS-*b*-PVME has a two-phase lamellar structure consisting of PI microdomains and mixed PS/PVME microdomains. Applying a drop of water onto the ultrathin sections induced further microphase separation between PS and PVME within the lamellar microdomains resulting in the three-phase structure. Water is a selective solvent for PVME and might have lowered the order–disorder temperature between PS and PVME. This step-wise microphase separation may be a new technique to control microphase-separated structures in triblock terpolymers. © 2002 Published by Elsevier Science Ltd.

Keywords: Triblock terpolymer; Step-wise microphase separation; Transmission electron microscopy

1. Introduction

Morphological studies of triblock terpolymers consisting of A, B and C blocks have made remarkable progress in recent years because of rich varieties of ordered structures compared to diblock copolymers [1–7]. Some examples of the three-phase morphology of ABC triblock terpolymers were first given by Riess et al. [8] as the combinations of lamellar, cylindrical and spherical microdomains. Even for the combinations of only these three kinds of microdomains, at least 12 different morphologies can be considered [9] (Fig. 1). Although the models shown in Fig. 1 are nothing but a simple geometrical prediction, some of them have been experimentally observed already [8–12]. If one takes into account more complex microdomains such as a tri-continuous structure, the morphological variation expands tremendously. In fact, some extremely complex morphologies have been observed [12,13].

While recent studies revealed the existence of many interesting microdomain morphologies, an experimental attempt to investigate the phase behavior (order–disorder transition and order–order transition) and ordering process (order–disorder process and order–order process) of a triblock terpolymer have never been reported, to our knowledge, because of their complexity. However, clarification of them is a key issue for controlling and creating complex microdomain morphologies. Since we plan to carry out such studies in this field, we will first choose and synthesize the block copolymers suitable for the studies.

When we investigate the ordering process of a triblock terpolymer, we have to consider two cases. One is the case where three components in the triblock terpolymer simultaneously segregate from each other. The other is the case where one of the three component segregates from the other two (first-step) and then the remaining two components segregate from each other (second-step) within the nano-space confined by the microdomains having been formed in the first step as schematically illustrated in Fig. 2. For the latter case (step-wise ordering), the microphase separation in the first-step is similar to that of a diblock copolymer. In other words, the step-wise ordering simplifies

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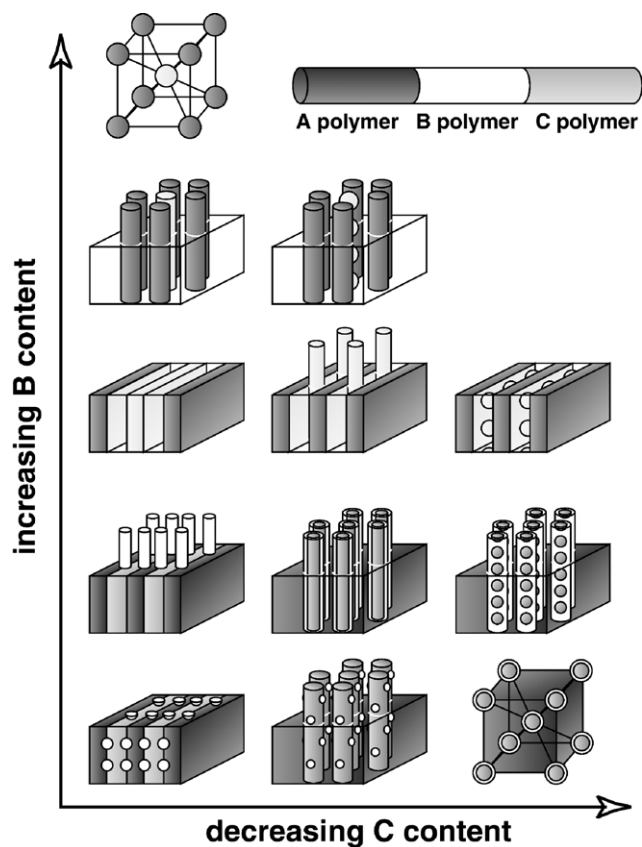


Fig. 1. Possible microdomain morphologies for three-phase structures of ABC triblock terpolymers composed of lamellar, cylindrical and spherical microdomains.

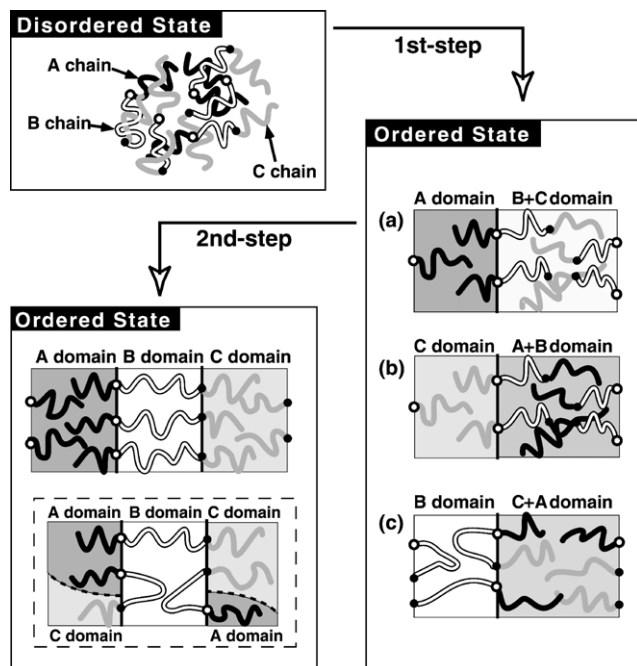
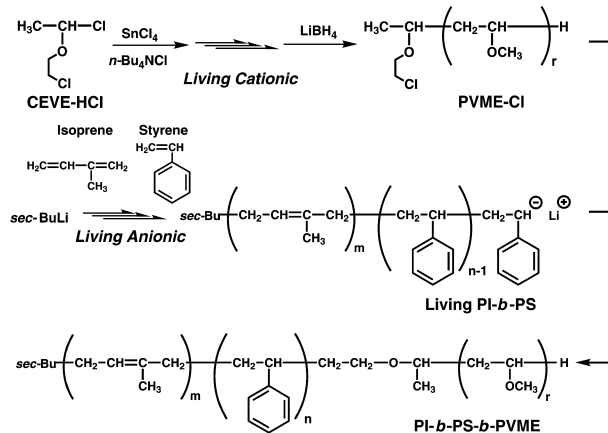


Fig. 2. Step-wise ordering of ABC triblock copolymer. One component microphase-separates from the others, and then the remaining two components microphase-separates from each other.

the complex ordering process of a triblock terpolymer by dividing it into two steps. As for the step-wise ordering of a triblock terpolymer, the second-step of the microphase separation has to proceed within the existing microdomain structures. Such situation occurs only when we adopt the system consisting of more than three components. Therefore, a triblock terpolymer ready to undergo a step-wise ordering has a large possibility for structure control.

For our purpose, one of the three components in our triblock terpolymer sample must segregate from the other two in the first-step of the step-wise ordering, while the remaining two components are still miscible. Moreover, this state must exist as a thermodynamically stable state. Polyisoprene-*block*-polystyrene-*block*-poly(vinyl methyl ether) (PI-*b*-PS-*b*-PVME) meets this condition because PS and PVME are miscible at room temperature while PI is immiscible with both PS and PVME. Therefore, PI-*b*-PS-*b*-PVME triblock terpolymer is expected to have a two-phase microdomain structure at room temperature, i.e. one phase composed of the PI block and the other composed of the PS and PVME blocks mixed. Such a state corresponds to the first-step of the step-wise ordering.

For the second-step, the PS and PVME blocks are possible to microphase-separate into two phases by two ways. One way is to increase temperature. Since a homopolymer blend of PS and PVME has a lower critical solution temperature (LCST)-type phase diagram [14–16], it is feasible that the PS and PVME blocks also undergo phase separation at high temperature. The other way is to apply a selective solvent. Since PS is a hydrophobic polymer and PVME is hydrophilic, water is a good solvent for PVME (at low temperature) but poor for PS. If the microdomains composed of PS and PVME blocks absorb water, they might undergo microphase separation. The absorbed water will enhance the effective segregation power between PS and PVME. In this study, we select the latter method to achieve the microphase separation between PS and PVME.



Scheme 1. Synthesis of PI-*b*-PS-*b*-PVME by coupling reaction of living PI-*b*-PS and PVME-Cl.

We adopted the methodology [17] to synthesize well-defined PI-*b*-PS-*b*-PVME triblock terpolymers, as illustrated in Scheme 1. This methodology consists of two steps: the synthesis of an end-chlorinated poly(vinyl methyl ether) (PVME-Cl) carrying a primary alkyl chloride terminal and the synthesis of living anionic PI-*b*-PS, followed by their coupling reaction. PVME-Cl can be obtained by the living cationic polymerization of vinyl methyl ether (VME) initiated with the hydrogen chloride adduct of 2-chloroethyl vinyl ether (HCl-CEVE), which is regarded as a functionalized initiator with a 2-chloroethyl group that can effectively quench polystyryl carbanions. The HCl-CEVE initiator is combined with SnCl₄ as a Lewis acid-type activator in conjunction with an added *n*-Bu₄NCl salt in dichloromethane (CH₂Cl₂) solvent at -78 °C. Because this system induces living polymerization of VME [18], as demonstrated in this work as well, the resulting polymer has a terminal chloroethyl group derived from the initiator, in addition to a controlled molecular weight distribution (MWD). The living PI-*b*-PS anions were prepared by the conventional sequential living anionic polymerization of isoprene and styrene with *sec*-butyllithium (*sec*-BuLi).

In this paper, we report the synthesis of well-defined PI-*b*-PS-*b*-PVME sample via the coupling reaction of the preparation of a PVME-Cl with a living PI-*b*-PS (Scheme 1).

We introduce an initial study of the microdomain morphologies by transmission electron microscopy (TEM) in this paper.

2. Experimental

2.1. Materials

Vinyl methyl ether (Daicel Chemical Industries, Ltd; purity > 98%), commercially obtained in a small gas cylinder, was condensed under dry nitrogen at -78 °C just before use into a baked graduated glass tube equipped with a three-way stopcock, where the liquefied monomer was diluted with CH₂Cl₂ into a stock monomer solution at a known concentration. 2-Chloroethyl vinyl ether (Nisso Maruzen Chemical; purity > 99.5%) was washed with aqueous 10% sodium hydroxide solution and then with water, dried overnight with anhydrous sodium sulfate, and distilled twice over calcium hydride under atmospheric pressure. Styrene monomer (Nacalai Tesque; purity > 99%) was purified by aluminum oxide for a few hours. Isoprene monomer (Nacalai Tesque; purity > 98%) was purified by molecular sieves for a few hours. Solutions of SnCl₄ (1.0 M in CH₂Cl₂), *sec*-BuLi (1.0 M in cyclohexane) and Bu₂Mg (1.0 M in heptane), all from Aldrich, were used as received. Commercial *n*-Bu₄NCl (Nacalai Tesque; purity > 95%) was used as supplied after drying under vacuum at room temperature. The initiator (HCl-CEVE) was prepared by electrophilic addition of hydrogen chloride to CEVE in *n*-

hexane, as reported previously [19,20]. Benzene and CH₂Cl₂, both from Nacalai Tesque, were dried overnight over molecular sieves.

2.2. Polymerization procedures

The polymerization of VME, isoprene and styrene and the coupling reaction were carried out under dry nitrogen atmosphere in a baked glass tube equipped with a three-way stopcock and a magnetic stirring bar. All reagents were transferred into the vessel via dried syringes through the three-way stopcock against a dry nitrogen stream.

A typical example of the living cationic polymerization of VME was as follows: to a VME solution (220 mM, 17 ml) in CH₂Cl₂ cooled at -78 °C with vigorous stirring added were a solution of the initiator HCl-CEVE (1.0 M, 2.0 ml; in CH₂Cl₂) and then a solution of SnCl₄ and *n*-Bu₄Cl (100 mM each, 5.0 ml; in CH₂Cl₂). The reaction was quenched with LiBH₄ (2.0 ml).

The quenched reaction solution was diluted with benzene and washed sequentially with diluted hydrochloric acid, an aqueous sodium hydroxide solution, and water to remove the tin-containing residues, where the washing solutions were used above 40 °C to avoid loss of the product polymer, PVME-Cl. The organic layer was evaporated to dryness under reduced pressure and dried under vacuum overnight to give the product PVME-Cl. Apart from aliquots for analysis; the PVME-Cl samples for the coupling reaction were dissolved in 1,4-dioxane and freeze-dried.

A typical example of the living anionic polymerization of isoprene and styrene were as follows [21]: under dry nitrogen via the syringe technique, a solution of *sec*-BuLi (1.03 M, 0.67 ml) was added to a solution of isoprene (98.4 mM, 9.83 ml) in benzene at 50 °C to give a colorless solution of isoprene anion. Styrene (32.1 mM, 3.68 ml) was added to this to give an orange solution typical for the polystyryl anion.

The polymerization was run for 2 h each for isoprene and styrene when the colorless solution turned to orange. Before the coupling reaction, Bu₂Mg (1.0 M, 3.68 ml) was added to the benzene solution of PVME-Cl for purification to give a yellow solution. For the coupling reaction, the benzene solution of PVME-Cl was added to the solution of the living PI-*b*-PS prepared above. The mixture immediately turned to light yellow and it was stirred for an additional 1 h. The quenched solution was diluted with benzene and washed with water to remove the residues (LiCl and Bu₂Mg) and the product polymer was further treated by freeze-drying.

Part of the living PI and the living PI-*b*-PS solution (1.0 ml) were separately quenched with methanol, and the homopolymer and the diblock copolymer were recovered for the MWD analysis by the same method as that for the product polymers.

2.3. Characterization of samples

The molar mass of the polymers and the MWD were

characterized by gel permeation chromatography (GPC). In each synthesis precursory samples were taken out before the next step polymerization to determine their molar mass. The number-average molecular weight M_n and polydispersity index M_w/M_n values of the polymers were calculated from GPC on the basis of PS calibration.

A further structural elucidation of PI-*b*-PS-*b*-PVME was performed by a combined GPC and reversed phase high pressure precipitation liquid chromatography (RP-HPPLC) technique, abbreviated as HPLC–GPC coupling hereafter. Characteristic for the applied technique is initial separation according to chemical composition by HPLC followed by multiple detection GPC of on-line taken HPLC eluate samples. Method and computer program for automated measurement and data processing is based on ideas of one of us (Konrad Knoll) and has been written in order of BASF by co-operation of hs GmbH (Ober-Hilbersheim, Germany) and Polymer Standards Service GmbH, Mainz, Germany [22–25]. Off-line measurements usually in the order GPC–HPLC and theories of the different HPLC separation techniques of polymers have been described earlier [26].

2.4. Transmission electron microscopy

The microdomain structures in the as-cast films of PI-*b*-PS-*b*-PVME and (PI-*b*-DPS-*b*-PVME) triblock terpolymers were observed under a transmission electron microscope. The film specimens were prepared by casting from a 5 wt% polymer solution in toluene. The dried film specimens were ultramicrotomed with a glass knife under a dry condition at $-80\text{ }^\circ\text{C}$ using a Reichert Ultracut E ultramicrotome equipped with a cryogenic sectioning unit before staining. The ultrathin sections were stained with the vapor of 2% aqueous solution of osmium tetroxide (OsO_4) at room temperature for about an hour. Some of the sections were stained with 0.5 wt% aqueous solution of phosphotungstic acid (PTA). Electron microscopic observations were carried out with a JEOL JEM-2000FX transmission electron microscope operated at an acceleration voltage of 120 kV.

3. Results and discussion

3.1. Synthesis of PI-*b*-PS-*b*-PVME

Vinyl methyl ether monomer is polymerized by living cationic reaction, while PI-*b*-PS diblock copolymer is synthesized by living anionic reaction. The coupling reaction between end-functionalized PVME and PI-*b*-PS was used to synthesize PI-*b*-PS-*b*-PVME. For the studies of its phase behavior and self-assembling process, it is needed to synthesize well-defined samples by the living polymerization. We previously reported that the coupling reaction between living PS anion and PVME-Cl gave a well-defined polystyrene-*b*-poly(vinyl methyl ether) diblock copolymer (PS-*b*-PVME) useful for the phase behavior study by small-angle neutron scattering (SANS) [17]. Therefore, the same

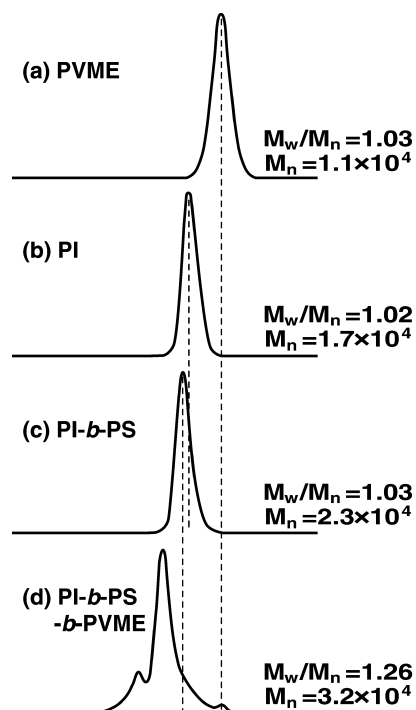


Fig. 3. GPC curves of ISV1: (a) PVME-Cl, (b) PI, (c) PI-*b*-PS and (d) PI-*b*-PS-*b*-PVME obtained with a RI detector.

technique is considered to be applicable for the synthesis of PI-*b*-PS-*b*-PVME. PVME-Cl was synthesized according to the route shown in Scheme 1. The polymerization of VME was initiated with the HCl-CEVE/ SnCl_4 system in the presence of $n\text{-Bu}_4\text{NCl}$ in CH_2Cl_2 at $-78\text{ }^\circ\text{C}$. Fig. 3(a) shows the GPC results of thus obtained PVME-Cl ($M_n = 1.1 \times 10^4$). This unimodal and narrow MWD ($M_w/M_n = 1.03$) suggest that the HCl-CEVE-based system led to the living polymerization of VME. Similarly, living PI-*b*-PS was synthesized according to the route shown in Scheme 1, in benzene at $50\text{ }^\circ\text{C}$ under dry N_2 atmosphere with *sec*-BuLi as initiator. Fig. 3(b) and (c) show the GPC curves for the PI and PI-*b*-PS precursors, both with very narrow MWDs ($M_w/M_n = 1.02$ and 1.03 , respectively).

The coupling reaction between the PVME-Cl and the living PI-*b*-PS was performed in benzene at $50\text{ }^\circ\text{C}$. PVME is a hydrophilic polymer and contains some bound water, which cannot be removed by the freeze-drying technique. This gives a serious effect to the coupling reaction because the living PI-*b*-PS reacts with water much faster than PVME-Cl, resulting in the deactivated PI-*b*-PS diblock copolymer/PVME homopolymer mixture. We found that *sec*-Bu₂Mg is very useful to remove water from PVME-Cl solution in benzene before the coupling reaction, because it does not react with living PI-*b*-PS. The benzene solution of the PVME-Cl with *sec*-Bu₂Mg was added drop-wise to the solution of the living PI-*b*-PS in benzene until the orange color of the living polystyryl anion disappeared. The GPC results of the product of the coupling reaction are shown in Fig. 3(d). A new major fraction with the peak molecular weight

Table 1
GPC characterization of ISV1

Sample	M_n	M_w/M_n	Composition ^a
ISV1	32,000	1.26	47:26:27

^a The volume ratio of PI:PS:PVME.

almost equal to the sum of the two prepolymers emerged. This fraction of the final product is considered as the PI-*b*-PS-*b*-PVME triblock terpolymer and designated as ISV1 hereafter. The minor fraction observed as the tail on the lower molecular weight side is most likely attributed to the deactivated PS-*b*-PI and/or PVME. As for the minor fraction observed as a small peak at higher molecular weight side will be clarified later.

3.2. Characterization of triblock terpolymers with 2D chromatogram of HPLC–GPC coupling

Table 1 shows the characterization data by GPC for the three triblock terpolymers synthesized in this study. ISV1, whose microdomain morphologies were studied, was further characterized by the HPLC–GPC coupling, and the amount of each species found in the 2D map is shown in Table 2.

In Table 2, the RI signal detects all polymers, but it is semi-quantitative due to the different refractive index increments of different polymer fractions. The UV signal reflects the distribution of the PS blocks over the different fractions. It was revealed by the HPLC–GPC coupling that seven kinds of polymers co-exist in the final products, i.e. ISV1 triblock terpolymer, PI and its coupling product PI–PI, the PI–PS diblock and its coupling product (PI–PS)₂, a product consisting of two PI-*b*-PS and one PVME ((PI–PS)₂ + PVME), and a product of three PI-*b*-PS and one PVME ((PI–PS)₃ + PVME).

The coupling products (PI–PI and (PI–PS)₂) might have been yielded by the leakage air when precursor polymer was sampled from the glass tube. As for the higher molecular weight fractions ((PI–PS)_{*n*} + PVME (*n*: integer)), it is considered that several PI–PS branches were grafted to PVME. The details of this grafting and its mechanism will be discussed in a subsequent paper.

Table 2
Characterization of the ISV1 triblock terpolymers with 2D chromatogram of HPLC–GPC coupling

Component	RI signal (%)	UV signal (%)
PI–PS–PVME	58.0	59.8
PI	5.7	0.3
PI–PS	12.2	14.3
PI–PI	1.7	0.3
(PI–PS) ₂	2.2	2.3
(PI–PS) ₂ + PVME	14.1	16.3
(PI–PS) ₃ + PVME	2.9	3.6

3.3. TEM observations

The microdomain morphology and the phase transition of ISV1 were investigated by TEM. Fig. 4(a) shows the TEM micrograph for the ultrathin section cut from the as-cast film of ISV1 stained with OsO₄. The structure with alternating dark and bright stripes implies a lamellar morphology. Since OsO₄ stains only the PI component, the bright phase may be composed of PS and PVME component. The volume ratio of PI/PS/PVME = 47:26:27 estimated from the characterization data agrees with the thickness ratio of the dark and bright layers ~50:50. According to our previous result, PVME-*b*-DPS with the molecular weight of 2.3×10^4 and the DPS volume fraction of 0.27 was miscible at all observed temperatures up to 206 °C [17]. Therefore, it is quite possible that the PS and PVME blocks are mixed in the bright layers in Fig. 4(a). However, it is not possible to confirm it from this picture alone.

Next, we carried out the double staining, i.e. the ultrathin section stained with OsO₄ was further stained with 1% aqueous solution of PTA at room temperature for 15 min. It is known that PTA stains the PVME phase selectively when it is segregated from PI and PS components [27]. If the PS and PVME components had been microphase separated within the bright layer in Fig. 4(a), the PVME microdomain should have been stained dark by PTA. However, the ultrathin section observed after the PTA staining did not show any change, though the corresponding TEM image was not shown here. This result confirms that PS and

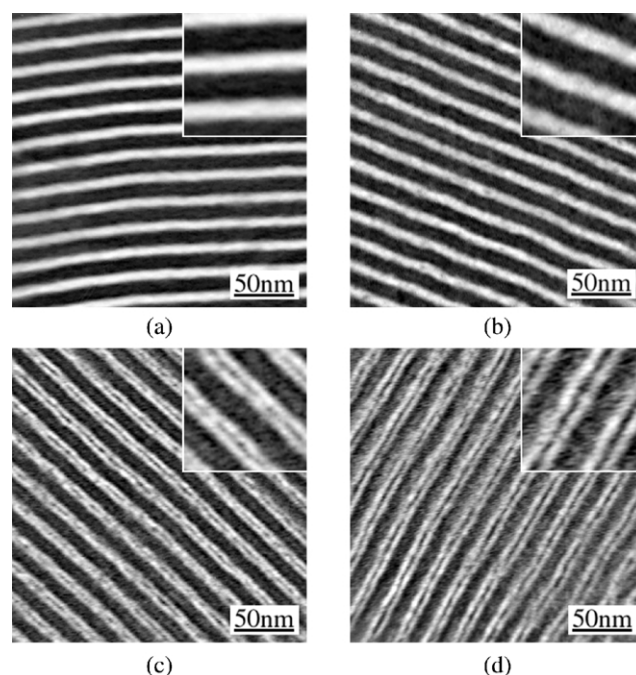


Fig. 4. TEM images of ISV1 film. All the images were obtained first by staining with OsO₄ and followed by staining with PTA. Difference from part (a) to part (d) is the time exposed to purified water before staining with PTA. (a) 0 min. (b) 30 min. (c) 45 min. (d) 60 min. The inset pictures are the enlarged images of the corresponding microdomain structures.

PVME blocks are mixed together to form a single microphase in the as-cast film.

In our previous work [17], we showed that PVME-*b*-DPS exhibited a LCST-type behavior, i.e. the segregation power between PVME and DPS increased with increasing temperature as for the case of PVME/PS homopolymer blends. On the other hand, PVME-*b*-DPS is an amphiphilic block copolymer, PVME is hydrophilic and DPS (and PS) is hydrophobic. It has been known that the moisture absorbed by PVME/PS homopolymer blends considerably lowers the phase-separation temperature [28]. Therefore, it is expected that water should enhance the segregation power between the PS and PVME blocks in ISV1. If we apply the PTA solution onto the ultrathin section for a longer time, the water in the solution may drive the microphase separation between the PS and PVME blocks and new PVME domains stained by PTA may appear. In such a case, however, it is difficult to distinguish the following two cases: (i) the microphase separation is driven by water, and (ii) PS and PVME are microphase-separated in the as-cast film but staining with PTA needs a time longer than 15 min. Therefore, we put a drop of purified water onto the ultrathin sections for 30, 45 and 60 min, removed the water with a piece of filter paper, and then applied and stained with the PTA solution for 15 min. The resulting TEM micrographs are shown in Fig. 4(b)–(d).

After 30 min treatment with water, no change was observed as shown in Fig. 4(b). However, after 45 min treatment with water, dark discontinuous domains appeared within the bright layers as shown in Fig. 4(c), suggesting the segregation of the PVME component, and finally after 60 min new thin dark layers of the PVME-rich phase appeared in the center of the bright layers of the PS-rich phase as shown in Fig. 4(d). It is considered that 30 min treatment with water is not enough to promote the microphase separation between the PS and PVME blocks. The microphase separation seems to start between 30 and 45 min after applying water to the specimen and a well-defined three-phase lamellar structure with a repeat unit of PI (dark, thick)–PS (bright)–PVME (dark, thin)–PS (bright) seems to be fully developed after 60 min. This may be the first observation of the second-step microphase separation in triblock terpolymers although the experiment was limited to the extremely thin films.

In Fig. 4, the ultrathin sections were stained with OsO₄ first and then water was applied onto them. Therefore, the PI blocks were tightly cross-linked [29] after the reaction with OsO₄ and the second-step microphase separation took place under a constraint that the PI microdomains are fixed in terms of their thickness and interfacial area. If the PI component is not cross-linked, a different morphology may be observed after the second-step microphase separation of PS and PVME block chains. Such a condition may be realized by applying water or aqueous PTA solution onto the ultrathin sections of the as-cast film before staining with OsO₄. Fig. 5(a) shows the TEM micrograph for the ultrathin

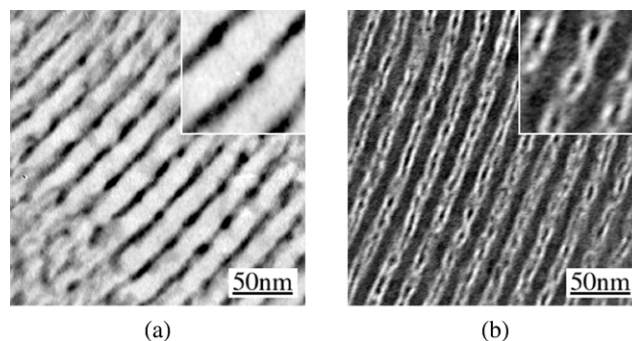


Fig. 5. TEM images of ISV1 film: part (a) is PTA-stained ultrathin section, part (b) is the ultrathin section stained with PTA and then OsO₄. The inset pictures in parts (a) and (b) are the enlarged images of the observed corresponding images.

section stained with the PTA solution for 15 min. The dark regions correspond to the PVME-rich phase selectively stained with PTA, while unstained PI and PS-rich phases appear bright. This picture indicates that 15 min exposure of the ultrathin section to the aqueous solution of PTA is enough for the PS and PVME blocks to microphase-separate. This time interval required for the PTA staining is considerably shorter than that in the case of the PI phase being fixed by the cross-links with OsO₄. As for the microdomain morphology of Fig. 5(a), some of the PVME-rich domains appear like lamellar structures, but most of them were discontinuous and appear like arrays of spheres or cylinders. Fig. 5(b) shows the TEM micrograph of the doubly stained (first with PTA, and then with OsO₄) ultrathin section. The pattern with dark and bright stripes resembles that of Fig. 4(d). Although the PI phase forms lamellar microdomains, their interfaces are wavier than those in Fig. 4(d). This waviness of the interfaces could have resulted from the waviness of the domains developed in the second-step microphase separation between the PS and PVME blocks. The second-step microphase separation involves a considerable rearrangement of the block chains and should have affected the interfaces between the PI phase and the PS/PVME mixed phase. Since the PI domains were not fixed by the cross-links in this case, the interfaces must have easily deformed and flowed and the PS and PVME blocks must have had more freedom on the microphase separation in contrast to the case of Fig. 4(d). This might have influenced the final morphology of the PVME microdomains such as shown in Fig. 5(b), i.e. the PVME microdomains do not form continuous lamellar structure such as those in Fig. 4(d) but rather tend to form cylindrical or spherical microdomains in the PS microdomains as schematically shown in one of the possible morphologies in Fig. 1 (the middle or right morphology in the third row). However, it should be noted that this morphology itself may suffer non-equilibrium effects as a consequence of vitrification of the PS domains accompanied by the second-step microphase separation.

We could confirm that ISV1 shows the step-wise ordering, namely, PI is immiscible with both PS and PVME at room temperature, so that the co-polymer is separated into two microphases, PI phase and the mixed phase of PS and PVME. In this study, water causes the second-step microphase separation between PS and PVME, because the PS and PVME block copolymer are amphiphilic.

We believe that ISV1 provides a good model system for the analysis of phase transitions and domain formations of ABC triblock terpolymers. It is particularly intriguing to study a role of competing short-range interactions among PI/PS, PI/PVME which have a UCST-type phase diagram and PS/PVME which give a LCST-type phase diagram on final morphology and phase transitions.

4. Conclusions

We successfully synthesized PI-*b*-PS-*b*-PVME triblock terpolymers by the coupling reaction between end-chlorinated PVME (PVME-Cl) and living PI-*b*-PS diblock copolymer anion (or living PI-*b*-DPS anion). A precise characterization of the reaction product based on the GPC and the 2D chromatogram of the HPLC–GPC coupling revealed that the product polymer contains traces of unreacted PVME-Cl, deactivated PI and PI-*b*-PS diblock copolymer and higher molecular weight species comprised of PI-*b*-PS-*b*-PVME reacted with PI-*b*-PS blocks besides the dominant fraction of the triblock terpolymer.

The TEM on the ultrathin sections of toluene-cast film of a PI-*b*-PS-*b*-PVME (ISV1) stained with OsO₄ and subsequently with aqueous solution of PTA revealed a two-phase lamellar structure, dark PI phase stained by OsO₄ and unstained bright mixed phase of PS and PVME. By applying first a drop of water to the OsO₄-stained ultrathin section for 60 min and then the PTA solution, a new dark layer of PVME phase stained with PTA appeared in the center of the bright PS phase which was also sandwiched by the dark PI layer. Thus we observed for the first time the step-wise microphase separation in a triblock terpolymer: the first step microphase separation occurred between one component (PI) and the other two (PS and PVME) during solution casting process, and the second-step microphase separation was induced by water, which lowered the order–disorder transition temperature of the miscible pair (PS and PVME blocks). The second-step microphase separation occurred in between the nano-space confined by the PI lamellar microdomains which were fixed by cross-links after the reaction with OsO₄ and, therefore, the second-step microphase separation was significantly affected by this constraint induced by the cross-links. The second-step microphase separation free from the cross-linking constraint was clarified to yield slightly different morphology in the text.

The step-wise microphase separation may be a new tech-

nique to control triblock terpolymers because the first-step resembles the microphase separation in diblock copolymers and we already have enough knowledge about the structure control. Next research subject is the systematic investigation of the second-step microphase separation within the microdomain space.

PI-*b*-PS-*b*-PVME is an extremely interesting system because PS and PVME have a LCST-type phase diagram while PI and PS (or PVME) have an UCST-type phase diagram. The competition of these three order–disorder transitions with temperature and/or pressure makes the phase behavior extremely rich but complex. However, it can be investigated by using a combined SAXS and SANS analysis, because they give a different contrast for the three components and, therefore, the complementary information. The study along this line is now in progress and will be presented in subsequent papers.

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References

- [1] Bates FS, Fredrickson GH. *Phys Today* 1999;52:32.
- [2] Birshstein TM, Zhulina EB, Polotsky AA, Abetz V, Stadler R. *Macromol Theor Simul* 1999;8:151.
- [3] Goldacker T, Abetz V, Stadler R, Erukhimovich IY, Leibler L. *Nature* 1999;398:137.
- [4] Goldacker T, Abetz V. *Macromolecules* 1999;32:5165.
- [5] Goldacker T, Abetz V. *Macromol Rapid Commun* 1999;20:415.
- [6] Abetz V, Goldacker T. *Macromol Rapid Commun* 2000;21:16.
- [7] Goldacker T, Abetz V, Stadler R. *Macromol Symp* 2000;149:93.
- [8] Riess G, Schlienger M, Marti S. *J Macromol Sci Polym Phys Ed* 1980;B17:355.
- [9] Tanaka Y, Hasegawa H, Hashimoto T, Ribbe A, Sugiyama K, Hirao A, Nakahama S. *Polym J* 1999;31:989.
- [10] Kudose I, Kotaka T. *Macromolecules* 1984;17:2325.
- [11] Stadler R, Auschra C, Beckmann J, Krappe U, Voigt-Martin I, Leibler L. *Macromolecules* 1995;28:3080.
- [12] Mogi Y, Mori K, Matsushita Y, Noda I. *Macromolecules* 1992;25:5412.
- [13] Breiner U, Krappe U, Thomas EL, Stadler R. *Macromolecules* 1998;31:135.
- [14] Kwei TK, Nishi T, Roberts RF. *Macromolecules* 1974;7:667.
- [15] Nishi T, Wang TT, Kwei TK. *Macromolecules* 1975;8:227.
- [16] Nishi T, Kwei TK. *Polymer* 1975;16:285.

- [17] Hashimoto T, Hasegawa H, Hashimoto T, Katayama H, Kamigaito M, Sawamoto M, Imai M. *Macromolecules* 1997;30:6819.
- [18] Ohmura T, Sawamoto M, Higashimura T. *Macromolecules* 1994;27:3714.
- [19] Katayama H, Kamigaito M, Sawamoto M, Higashimura T. *Macromolecules* 1995;28:3747.
- [20] Higashimura T, Kamigaito M, Kato M, Hasebe T, Sawamoto M. *Macromolecules* 1993;26:2670.
- [21] Creutz S, Vandooren C, Jerome R, Teyssie P. *Polym Bull* 1994;33:21.
- [22] Kilz P. *GIT Labor Praxis* 1992;6:628 The co-authorship of K.K. is not indicated in the article due to secrecy reasons existing at that time.
- The experimental setup described there was now also used to analyze the PI-*b*-PS-*b*-PVME triblock terpolymers.
- [23] Kilz P, Krüger RP, Much H, Schulz G. *Adv Chem Ser* 1995;247:223.
- [24] Pasch H, Kilz P. *GIT Labor-Fachzeitschrift* 1999;43:239.
- [25] Schupp W. *GIT Labor-Fachzeitschrift* 1999;43:812.
- [26] Glöckner G. *Gradient HPLC of copolymers and chromatographic cross-fractionation*. Berlin, Germany: Springer, 1991.
- [27] Iizuka N, Bodycomb J, Hasegawa H, Hashimoto T. *Macromolecules* 1998;31:7256.
- [28] Hashimoto T, Itakura M, Shimidzu N. *J Chem Phys* 1986;85:6773.
- [29] Ribbe A, Bodycomb J, Hashimoto T. *Macromolecules* 1999;32:5154.