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Preparation and characterization of ABB graft copolymers

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Poly(2-vinylpyridine-*g*-styrene)s were prepared by successive coupling reactions of polystyryl anion and poly-2-vinylpyridinyl anion prepared by anionic polymerizations, with trifunctional coupling agent, tris-bromomethylbenzene. Five samples were prepared and characterized. Their volume fractions of polystyrene graft, ϕ_s, were determined to be 0.24, 0.34, 0.45, 0.58 and 0.67, respectively. Morphologies of the solvent-cast films of the samples were observed by transmission electron microscopy and small-angle X-ray scattering. It was revealed that two samples, with ϕ_s of 0.24 and 0.34, show cylindrical structures, while the other three samples have alternating lamellar structures.

(Keywords: graft copolymer; anionic polymerization; coupling reaction)

INTRODUCTION

Most of the morphological studies of copolymers have been focused on the microphase separation structures of block copolymers, and a large number of publications have accumulated. Linear AB diblock copolymers have been studied the most, both experimentally[1-4] and theoretically[5-8], because they are the simplest block copolymers and have the most basic microdomain structures.

The primary structural feature of diblock copolymers is that the different block components are chemically connected in a one-to-one arrangement at one junction point. In other words, the block chains are positioned symmetrically with regard to the domain boundary in microphase separation structures. On the other hand, a peculiar feature of graft copolymers is graft branching, so that graft and backbone chains are connected in a one-to-two arrangement at one junction point and hence they are asymmetrical in chain distribution at the domain boundary. Therefore, it is very interesting and worthwhile to study the microphase separation structures of graft copolymers, focusing on microdomain boundaries, in comparison with those of block copolymers.

However, in general, it is not easy to obtain well-defined graft copolymers. Recently, the term 'miktoarm' polymer was proposed, and a styrene–isoprene–isoprene (SII) star-shaped copolymer was prepared and its morphology examined[9]. In this work we report the procedure for preparing the simplest graft copolymers with definite structures, that is, star-shaped copolymers of the ABB type, and also report their microphase separation structures. Polystyrene and poly(2-vinylpyridine) were chosen as component polymers because several fundamental physical properties of these polymers, for example, statistical segment lengths and glass transition temperatures, are close to each other, although they are incompatible[10-12].

EXPERIMENTAL

Sample preparation

Graft copolymers were prepared by a coupling reaction between polystyrene (PS) with functional end group and carbanion living ends of poly(2-vinylpyridine) (P(2VP)). The preparation was carried out stepwise according to the following scheme:

$$\mathrm{PSLi} + \mathrm{CH_2} = \mathrm{C(C_6H_5)_2} \rightarrow \mathrm{PS(DPE)Li}$$

$$\mathrm{PS(DPE)Li} + \text{excess } \mathrm{C_6H_3(CH_2Br)_3}$$

$$\rightarrow \mathrm{PS(DPE)CH_2(C_6H_3)(CH_2Br)_2} + \mathrm{LiBr}$$

$$\mathbf{I}$$

$$\mathbf{I} + 2\mathrm{P(2VP)K} \rightarrow [\mathrm{PS(DPE)}][\mathrm{P(2VP)}]_2 + 2\mathrm{KBr}$$

Firstly, styrene was polymerized with sec-butyllithium as an initiator in toluene at 30°C using a break-seal method under high vacuum. Styrene monomer was purified with sodium benzophenone under vacuum and toluene was

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[§] Present address: Tokai Rubber Industries Ltd, 3600 Utazu, Kitatoyama, Komaki, Aichi 485, Japan purified with n-butyllithium, both after drying over calcium hydride. A small amount of polymerization solution was taken out as a precursor for molecular characterization as described below. Then, the living ends were capped with diphenylethylene (DPE) for 1 h at 25°C. (In our first attempt, polystyryl anions were terminated directly with 1,3,5-tris-bromomethylbenzene (TRBB) molecules and, surprisingly, the major product was star molecules with three PS arms, but not PS with bifunctional end groups, even though the molar ratio of added TRBB to living anion was more than two. We stirred the reaction solution overnight after adding DPE to living ends in our trial experiment and confirmed that the colour of the solution was quite stable after 30 min.) Since a slow colour change from golden yellow to dark cherry occurred during the first 30 min, but not the second 30 min, we considered that the addition reaction was almost completed during this reaction time. The living PS anions capped with DPE were terminated instantly at −78°C with an excess amount of TRBB (molar ratio of TRBB/Li = 5/3), so as to produce PS with two bromomethyl groups on one end as a major product. DPE was purchased from Kishida Reagents Chemicals and was distilled over n-butyllithium after drying over calcium hydride. TRBB was synthesized according to the procedure in the literature[13] and purified by recrystallization from n-hexane/chloroform mixed solvent system. In the above reactions, DPE and TRBB were used as tetrahydrofuran (THF) solutions. PS with bifunctional end group was precipitated into methanol and rinsed with fresh methanol three times to remove residual TRBB completely and then dried. Fractionation was performed in benzene/methanol mixed solvent system so as to exclude polymers with molecular weights higher than that of the precursor; these polymers were produced by undesirable coupling reactions between one TRBB molecule and two or three PS molecules with living ends. The isolated and dried PS with bifunctional end group was dissolved in purified THF and precipitated into purified n-heptane under vacuum, to exclude the impurities which are active against living carbanions in the following coupling reaction, and then dried. Two PS precursors with different molecular weights were prepared by this procedure. They were dissolved in purified THF again and stored in ampoules under vacuum. One solution was divided into three parts and another into two parts.

Five P(2VP)s with different chain lengths were prepared with cumyl potassium as an initiator in THF at −78°C under vacuum, also using a break-seal method. 2-Vinylpyridine monomer was also purified with sodium benzophenone after drying over calcium hydride, while THF was dried over sodium wire and distilled over sodium anthracene followed by further purification with dipotassium salt of α-methylstyrene tetramer under high vacuum. Parts of polymerization solutions were also taken out as precursors for characterization. Then THF solutions of PS were added into each THF solution of the living P(2VP) at −78°C and stirred vigorously. The molar amounts of living ends of the P(2VP) were designed to keep 20% more than those of the bromomethyl group in every reaction in order to avoid the production of molecules having only one P(2VP) arm. The products were precipitated into n-hexane and dried. Homo-P(2VP) resulted from the procedure adopted, and homo-PS without functional end groups was excluded by fractional gel permeation chromatography (g.p.c.) performed with a Tosoh G5000H$_6$ column (21.4 mm diameter and 600 mm length). The solvent used was chloroform containing about 3 vol% of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), which was added to avoid the adsorption of polymers on gels[10]. The range of polymer concentrations, the flow rate and the injection volume were 0.25–0.4 g dl^{-1}, 5 ml min^{-1} and 5 ml, respectively.

Characterization

The number-averaged molecular weights of PS precursors and graft copolymers were measured in toluene, and those of P(2VP) precursors were measured in THF with a membrane osmometer (Hewlett Packard type 502) at 25°C. The apparent molecular weight distributions were estimated using a Tosoh gel permeation chromatograph (type 802A) with two GMH$_{XL}$ columns. The columns were operated at 38°C under a pressure of 40 kg cm^{-2} and the flow rate was 1.0 ml min^{-1}. The solvent was THF containing 5 vol% of TMEDA for the reason described above. The compositions of graft copolymers were determined by pyrolysis–gas chromatography (py-g.c.) using a fused-silica capillary column at 600°C. Details of the experimental conditions for py-g.c. will be reported elsewhere[14].

Morphological observations

Films for morphological observations were cast from 4 wt% THF solutions of polymers for four or five days. THF is a good common solvent for two component polymers. As-cast films were dried in a vacuum oven for four days and then annealed under vacuum at 150°C for a week. It was checked by g.p.c. that the films had the same molecular weight distributions as those of as-cast films after annealing treatment. Staining was carried out by placing the ultrathin sections of films, with 70 nm thickness, under vapour of the staining agent, osmium tetroxide. It is known that it lightly stains the P(2VP) phase giving rise to weak contrast against the unstained PS phase. Microphase separation structures of specimens thus obtained were observed with a JEOL transmission electron microscope (model 2000FX) operated at an accelerating voltage of 75 kV. Small-angle X-ray scattering (SAXS) measurements were also carried out with a Kratky U-Slit Camera (Anton Parr) equipped with a scintillation counter and a step scanner. The incident X-rays were irradiated parallel to the film surface. Details of the morphological measurements were reported in previous papers[12,15].

RESULTS AND DISCUSSION

Preparation and characterization

Figure 1 compares gel permeation chromatograms of a PS precursor at each step. *Figure 1a* shows the chromatogram of as-polymerized PS, while *Figure 1b* shows that of the polymer after adding DPE and terminating with TRBB. A small shoulder can be seen at the higher-molecular-weight side of the chromatogram in *Figure 1b*, which corresponds to the molecules with two or three arms. *Figure 1c* is the chromatogram of the purified PS precursor by fractionation. The curve in *Figure 1c* is quite similar to that in *Figure 1a*.

Figure 2 shows an example of gel permeation

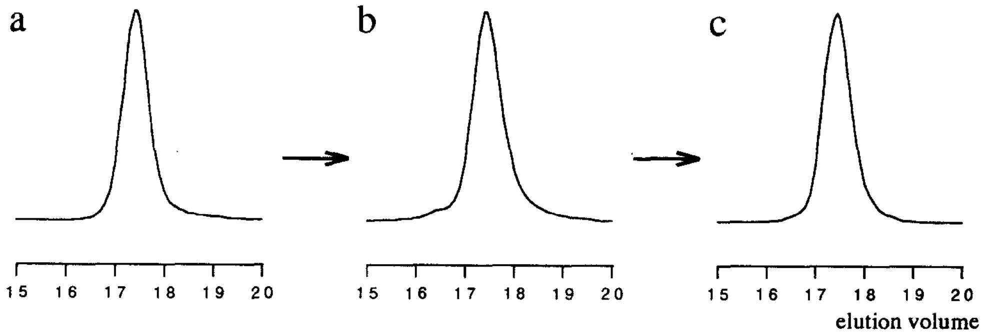

Figure 1 Comparison of gel permeation chromatograms of the PS precursor before and after coupling reaction with TRBB: (a) as-polymerized polymer; (b) polymer products after the coupling reaction; (c) purified polymer by fractionation

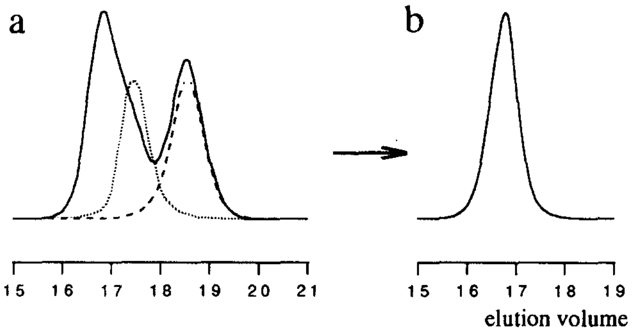

Figure 2 Comparison of gel permeation chromatograms of the SPP-3 graft copolymer before (a) and after (b) purification by fractional g.p.c.

chromatograms of a graft copolymer before and after purification by fractional g.p.c. The solid curve in *Figure 2a* denotes the polymer mixture after the coupling reaction for about 1 h, while the dotted and broken curves denote the PS and P(2VP) arms. We confirmed that the chromatogram of the reaction mixture after overnight stirring was similar to the solid curve in *Figure 2a*. This chromatogram clearly shows that the polymer obtained by the coupling reaction contains certain amounts of homo-PS and homo-P(2VP). The former may be produced during the coupling reaction between living PS and TRBB, probably because of impurities in the THF solution of TRBB; the latter was produced owing to the addition of the excess molar amount of living P(2VP), but its amount may be larger than expected because the molar amount of 'effective' PS, with two bromomethyl groups on one end, can be considered to be much less than the nominal amount calculated from the weight. On the other hand, *Figure 2b* shows the chromatogram of the purified graft copolymer which has a reasonably narrow molecular weight distribution, indicating that the isolation of the graft copolymer from the as-coupled polymer mixture was quite successful by fractional g.p.c.

Table 1 Molecular characteristics of graft copolymers

Sample code	$M_n \times 10^{-4}$ S	P	Graft	M_w/M_n	ϕ_s
SPP-1	5.35	8.90	22.5	1.03	0.24
SPP-2	5.35	6.47	17.9	1.03	0.34
SPP-4	9.25	5.65	20.6	1.04	0.45
SPP-3	5.35	2.49	9.52	1.03	0.58
SPP-5	9.25	2.54	14.2	1.05	0.67

Table 1 lists the molecular characteristics of five graft copolymers. The apparent molecular weight distributions are all fairly narrow and the measured number-averaged molecular weights of graft copolymers agree well with the sums of those of one PS and two P(2VP) precursors, within experimental error. Additionally, the measured volume fractions of PS arms, ϕ_s, are in good agreement with the values calculated from measured molecular weights of PS and P(2VP). From these facts we can conclude that five graft copolymers, with one PS arm at the centre of P(2VP) backbones but with different compositions, were obtained as designed.

Morphological observations

Figure 3 shows electron micrographs of three graft copolymers. It is clear from this figure that SPP-1 (*Figure 3a*) and SPP-2 (*Figure 3b*) have cylindrical structures, while SPP-5 (*Figure 3c*) has an alternating lamellar structure. SPP-3 and SPP-4 also had lamellar structures although they are not shown here. The results, with ϕ_s values of 0.24, 0.45 and 0.58 for SPP-1, SPP-4 and SPP-3, respectively, are consistent with the composition dependence of the microphase separation structures of styrene–isoprene (SI) diblock copolymers[4]. On the contrary, the fact that SPP-2, with $\phi_s = 0.34$, have a cylindrical structure and SPP-5, with $\phi_s = 0.67$, has a lamellar structure is apparently different from the case of SI diblock copolymers, in which a lamellar structure appears when $\phi_s = 0.34$, but alternatively polyisoprene forms cylinders in PS matrix when $\phi_s = 0.67$. However, the present result is consistent with that of Hadjichristidis *et al.*[9] on an SII miktoarm polymer with $\phi_s = 0.37$.

Figure 4 compares the SAXS intensity profiles of three samples. The top curve (SPP-1) in *Figure 4* is a typical diffraction pattern for the microphase separation structure of hexagonally packed cylinders in matrix, where the diffraction peaks appear at the relative positions of 1, $\sqrt{3}$ and $\sqrt{7}$ in terms of the scattering vector $q(= 4\pi \sin\theta/\lambda)$, where λ is the wavelength (0.154 nm) and 2θ is the scattering angle. On the contrary, the diffraction peaks appear at the relative position of 1, $\sqrt{4}$ and $\sqrt{7}$, but a peak at $\sqrt{3}$ is missing in the middle curve (SPP-2). These phenomena can be understood by considering the particle scattering functions, taking the radius of cylinders into account[16]. The first four possible reflections for hexagonally packed cylinders are [100], [110], [200] and [210], and their characteristic spacing ratios, d_{hk0}/d_{100}, are 1, $1/\sqrt{3}$, $1/\sqrt{4}$ and $1/\sqrt{7}$, respectively, where h and k denote the Miller indices and ds are the characteristic

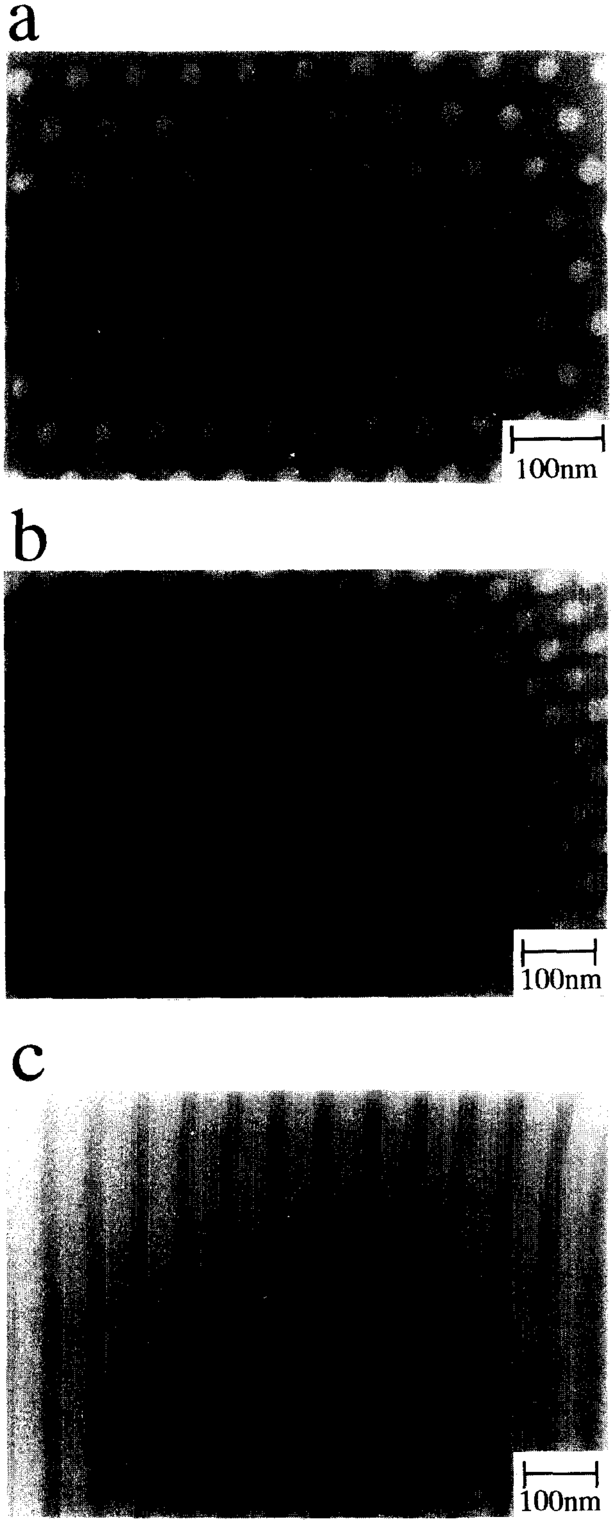

Figure 3 Typical electron micrographs of the samples: (a) SPP-1; (b) SPP-2; (c) SPP-5

spacings. In other words, the peaks should appear at the relative positions of 1, $\sqrt{3}$, $\sqrt{4}$ and $\sqrt{7}$ in terms of q, if d_{100} corresponds to the position of the first peak, q_{100}, according to the relation, $d_{100} = 2\pi/q_{100}$. The radius of cylinders, R, can be calculated by using d_{100} and ϕ_s thus obtained. The q values at the minima of the particle scattering factor are given as a function of R by:

$$qR = 3.83, 7.02, 10.17, \ldots$$

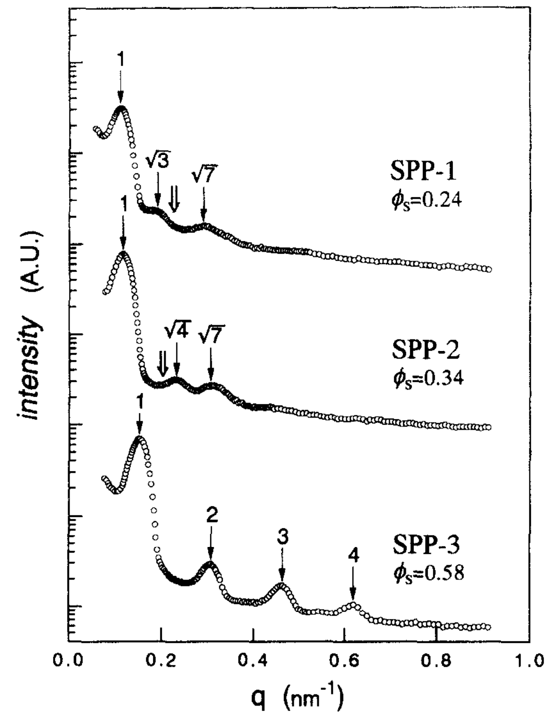

Figure 4 SAXS diffraction patterns of three samples

The positions of the first minima for SPP-1 and SPP-2 are indicated by the open arrows in *Figure 4*. Thee arrows explain the reason for the disappearance of peaks in the scattering profiles of two samples.

We are able to point out the essential difference in microphase separation structures between AB diblock copolymer and ABB graft copolymer when ϕ_A values are approximately 1/3 and 2/3. The difference in the morphologies may be attributed to the difference in chain dimensions along the direction parallel to the domain interface due to the difference in chain architectures; the total dimension of two B polymers of a graft copolymer along this direction is presumably larger than that of a B polymer of the block copolymer at the same composition. *Figure 5* shows schematically the difference in

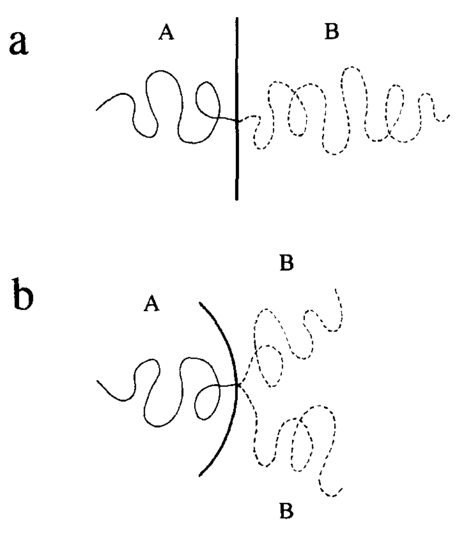

Figure 5 Schematic representation of chain conformations of an AB block copolymer (a) and an ABB graft copolymer (b) with the same ϕ_A of 1/3 in microphase separation structures

the possible conformations and shape of the domain boundaries between an AB diblock copolymer and an ABB graft copolymer with ϕ_A of 1/3 as an example. As shown in the figure, the microdomain interface of a graft copolymer becomes concave towards the A domain to keep the segment density of each domain constant. However, more extensive studies are required on samples with various compositions in order to clarify the composition dependence of the microphase separation structure of graft copolymers.

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