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Preparation and Morphology of Model Graft Copolymers of the A_3B_2 Type with Different Graft Junction Points

Atsushi TAKANO,[†,††] Kazunori KONDO, Masaya UENO, Kazuya ITO, Seiichi KAWAHARA, Yoshinobu ISONO, Jiro SUZUKI,[*] and Yushu MATSUSHITA[**]

Department of Chemistry, Nagaoka University of Technology, Nagaoka, Niigata 940–2188, Japan
[*]Neutron Scattering Laboratory, The Institute for Solid State Physics, The University of Tokyo, 7–22–1 Roppongi, Minato-ku, Tokyo 106–8666, Japan
[**]Department of Applied Chemistry, Nagoya University Furo-cho, Chikusa-ku, Nagoya 464–8603, Japan

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ABSTRACT: To investigate the effects of branching position on morphology of graft copolymers, a series of styrene-*g*-isoprene graft copolymers with the same backbone chain length and also with the same graft chain length but with different graft junction points was prepared by anionic polymerization applying a new preparation method in three steps; (1) coupling of living polystyrene onto telechelic polystyrene, (2) introduction of reactive but non-polymerizable vinyl groups onto the two connecting points of triblock polystyrene, (3) grafting of living polyisoprene onto polystyrene backbone with two reactive sites obtained in step (2). The samples were confirmed to have well-defined molecular structure as designed by characterization using osmometry, GPC, and ^{1}H NMR. Seven graft copolymers were prepared, which have almost the same total chain length, their constant polyisoprene volume fraction, ϕ_{PI}, being around 0.5. From morphological studies, the graft copolymers form cylindrical structures, not alternating lamellar structures, even though the volume fraction of graft chains is about 0.5. It turned out that domain spacing has minimum for a molecule whose two junction points divide backbone chain into three chains with the same chain length.

KEY WORDS Anionic Polymerization / Graft Copolymer / A_3B_2 Type / Morphology / Domain Spacing /

There are two major classes of multicomponent polymers, block and graft copolymers, consisting of different chemical sequences. Block copolymers exhibit microphase-separated structures in bulk, where ordered array of microdomains, that is, spherical, cylindrical, lamellar, and bicontinuous structures, appear turn by turn, depending on composition ratio.[1–6]

Limited studies have been reported on morphology of graft copolymers, mainly because precise syntheses of graft copolymers are hard to accomplish; therefore, detailed composition dependence of any series of graft copolymers has not been fully understood yet.[7–14] There are 4 structural parameters to specify the molecular architecture of graft copolymers: (I) graft chain length, (II) backbone chain length, (III) positions of branching points of grafts and (IV) number of grafts. To clarify features of graft copolymers mentioned above, several series of well-defined graft copolymers should be prepared systematically as shown in Figure 1. Such "model" graft copolymers, however, cannot be synthesized easily by conventional technique, since the reactants are mixture of the polymers having various molecular structures.

Recently, Matsushita *et al.*[10] and Pochan *et al.*[11] synthesized A_2B type graft copolymers, and reported their morphology. According to them, compositional dependence of microphase-separated structure of A_2B type graft copolymers is quite different from that of AB diblock copolymers.

However, the essential nature of a graft copolymer comes from the connection mode of graft chains onto

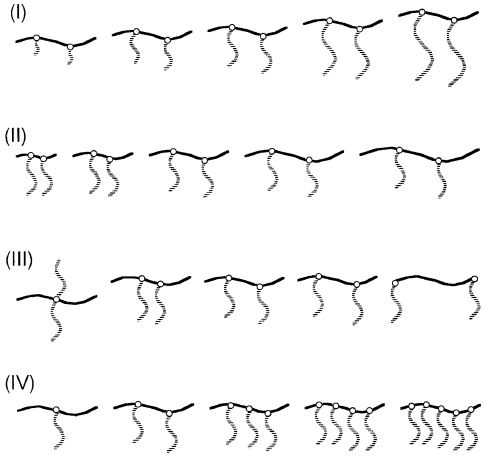


Figure 1. Schematic drawings of four series of model graft copolymers. Structural parameters to specify the molecular architectures of graft copolymers are (I) graft chain length, (II) backbone chain length, (III) positions of grafting points, and (IV) number of grafts.

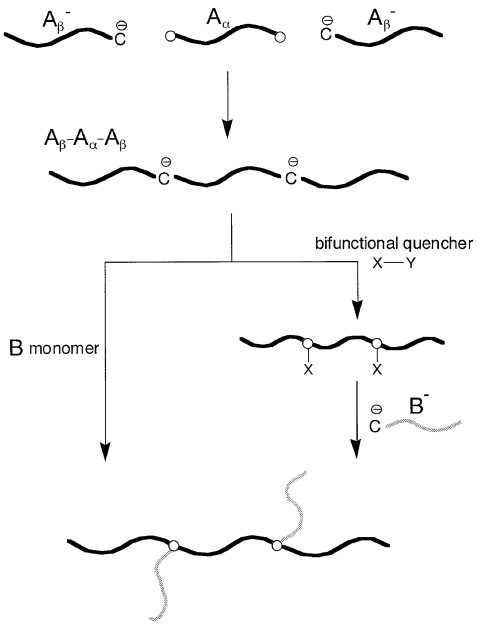
[†]To whom correspondence should be addressed.
[††]Present address: Department of Applied Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464–8603, Japan.

the backbone chain. In short, a backbone chain block between two adjacent grafting points posseses bridge and loop conformations. The simplest graft copolymer keeping this feature should consist of the three backbone blocks and the two grafts, hence it is called A_3B_2 type graft copolymer in this paper. A study on a graft copolymer of the A_3B_2 type has been recently reported by Gido *et al.*[12] They proposed a synthetic method using chlorosilane chemistry, where living A polymer was reacted with trifunctional coupler, and the obtained end-functional A polymer was reacted with living B, and finally the AB diblock polymer was coupled with a bifunctional living A polymer. Using this method, they prepared several samples, and investigated the compositional dependence of microphase-separated structure. To clarify the domain structure of graft copolymers of the A_3B_2 type at the molecular level, however, variation of morphology with the other structural parameters should be examined.

The first purpose of the present paper is to prepare graft copolymer samples of A_3B_2 type with different graft junction points adopting new preparation method for use of the successive morphological study. The controllable structural parameters for A_3B_2 type molecules are (I) graft chain length, (II) backbone chain length, and (III) branching positions when the number of grafts is fixed, two. To investigate the dependence of branching position on morphology, a series of graft copolymers with the same backbone chain length and also with the same graft chain length but with different branching positions as shown in Figure 1(III) was prepared. The variation of morphology of graft copolymers of A_3B_2 type with branching position has never been studied so far.

For systematic study, graft chains having the same chain length have to be introduced onto backbone polymers with the same chain length but with different reactive sites. Hence backbone polymers (A_β-A_α-A_β) having two reactive anionic sites at junction points were designed, as shown in Scheme 1. Such backbone polymers can be obtained by coupling reaction between telechelic macromonomers, A_αs and two living polymers, A_β^-s. The obtained A_β-A_α-A_β must not react with another macromonomer so as not to produce undesirable nonlinear backbone chain. Therefore we selected a vinyl group of the 1,1-diphenylethylene type which is known as the monomeric unit with inability of self-polymerization and shows high reactivity with most carbanions.

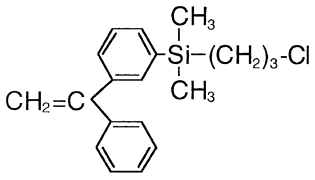
The reactive polymers, A_β-A_α-A_β, allow the introduction of graft chains in two different ways, one is the "grafting from method" which includes initiation and propagation of the other monomer B, while the other



Scheme 1.

is "grafting onto method" which means coupling with end-reactive polymers B. From an industrial viewpoint, the former method may be preferable, because the initiation and propagation reactions are faster than the interpolymer coupling reaction. The latter method, however, has superiority from the viewpoint of preparation of model graft copolymer, because precise characterization of both backbone polymer and graft chains in addition to graft copolymers can be easily achieved so that the latter method was adopted in this study.

To prepare telechelic macromonomers having 1,1-diphenylethylene-type vinyl groups, a new quencher having a 1,1-diphenylethylene-type vinyl group and a chloroalkyl group, (1-[3-(chloropropyldimethylsilylphenyl)-1-phenyl]ethylene, **I**) as described below has been synthesized. In the preparation of a telechelic macromonomer, a living polymer has to be end-capped by 1,1-diphenylethylene itself before treating **I** to prevent direct reaction between a living polymer and the vinyl group in **I**.



The second purpose of this study is to look for a cross-over point from block copolymer to graft copolymer, since the extreme case of this series can be considered as a block copolymer as is schematically drawn at the right end in Figure 1(III). Domain spacing of graft

copolymers is discussed quantitatively by comparing them with those of two extreme cases.

Polystyrene and polyisoprene were chosen as component polymers in this work because molecular weight and molecular weight distribution of these polymers were fully controllable using conventional living anionic polymerization under vacuum. They are incompatible enough and distinguishable by transmission electron microscopy (TEM) and small angle X-Ray scattering (SAXS).

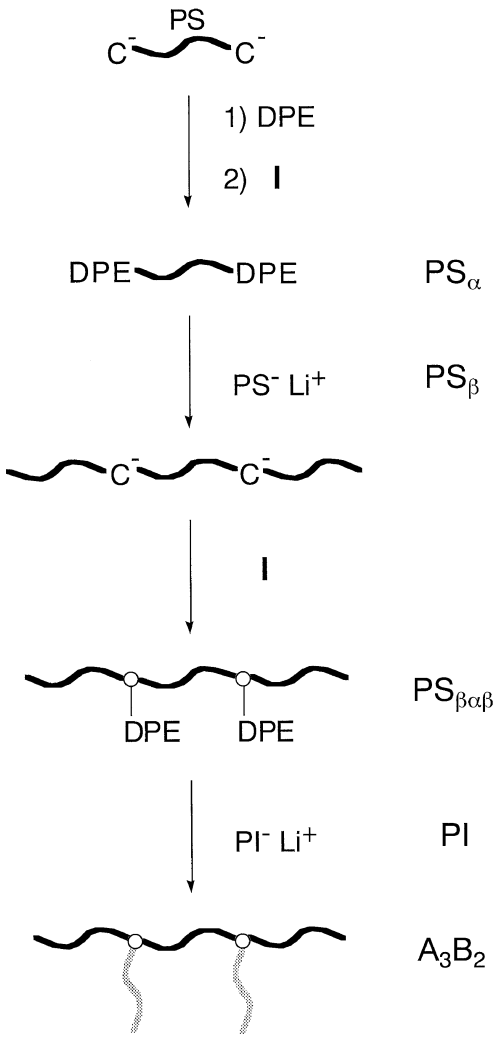
EXPERIMENTAL

*1-[3-(3-Chloropropyldimethylsilyl)phenyl]-1-phenylethylene (**I**)*

I was synthesized from 1-(3-bromophenyl)-1-phenylethylene (**II**) and 3-chloropropyldimethylchlorosilane (**III**). **II** was prepared by reaction of 3-bromoacetophenone with phenylmagnesium bromide followed by hydrolysis and dehydration in 65% yield. **II** (88 g, 0.34 mol) dissolved in THF (250 mL) was added dropwise to magnesium turnings (9.5 g, 0.40 mol) under nitrogen gas at 337 K for 2 h to give the Grignard reagent. After filtration, **III** (60 g, 0.35 mol) was added to the Grignard reagent and stirred at 293 K for 12 h. Fractional distillation of the product at 433–436 K under 133 Pa gave 94 g (0.30 mol) of **I** in 87% yield from **II**. The product was confirmed to be **I**: 400 MHz ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 6H, CH_3Si), 0.78 (t, 2H, $-CH_2-Si$), 1.70 (quint, 2H, $C-CH_2-C$), 3.40 (t, 2H, $Cl-CH_2-$), 5.40 (d, 2H, $CH_2=C$), 7.20–7.46 (m, 9H, C_6H_4+ C_6H_5). Purification of **I** was carried out in an all-glass apparatus equipped with breakseals under a pressure of 1×10^{-3} Pa or lower. After being dried with calcium hydride, **I** (42 g, 0.13 mol) was transferred into a vacuum apparatus and purified by distillation *in vacuo* at a bath temperature of 423 K. Finally **I** was diluted to 6 (v/v)% with purified THF.

Initiators, Solvents, Monomers, and Quencher

Sec-Butyllithium was purchased from Asia Lithium Co. Ltd. and was diluted with purified *n*-heptane. Lithium naphthalenide was synthesized by reaction between naphthalene and lithium turnings in THF at room temperature *in vacuo* for 5 min. Concentrations of initiators were determined by titration with standard HCl solution. Solvents, styrene, and isoprene monomers, and 1,1-diphenylethylene (DPE) were purified in the same manners as reported previously.[16, 17] Methanol was dried over calcium hydride.



Scheme 2.

Preparation of A_3B_2 Type Graft Copolymer

A_3B_2 type graft copolymer was prepared *via* four steps as shown in Scheme 2. All operations were carried out in a sealed glass apparatus with breakseals under a pressure of 1×10^{-3} Pa or lower. To prepare a telechelic polystyrene having DPE type vinyl groups at both chain ends, PS_α, styrene was anionically polymerized with lithium naphthalenide in THF at 195 K for 1 h to give bifunctional polystyryllithium which was endcapped with DPE at the ratio of [DPE]/[Li] = 3/1, followed by termination with **I** at the ratio of [**I**]/[Li] = 3/1 at room temperature. The polymer obtained was purified by precipitation from THF solution into an excess amount of methanol three times. Residual DPE and **I** was removed with *n*-hexane in a soxhlet extractor. After being freeze-dried, PS_α was transferred into a vacuum apparatus and diluted with purified THF. Monofunctional polystyryllithium, PS_β^-, was prepared with *sec*-BuLi in THF at 195 K. The PS_β^- was allowed to react with PS_α at the ratio of $[PS_\beta^-]/[PS_\alpha] = 5/1$ at 195 K

for 12 h to give polystyrene having two anionic sites, $PS_{\beta\alpha\beta}^{2-}$. After residual living PS_{β}^{-} was end-capped with DPE, DPE type vinyl groups were introduced onto $PS_{\beta\alpha\beta}^{2-}$ by addition of **I** at the ratio of [**I**]/[Li] = 3/1 so as to give nonionic reactive polystyrene backbone, $PS_{\beta\alpha\beta}$. Polyisoprenyllithium, PI^{-}, was prepared with *sec*-BuLi in *n*-hexane at room temperature. The solvent, *n*-hexane, was exchanged into THF after polymerization. Graft copolymer was prepared by coupling of $PS_{\beta\alpha\beta}$ with PI^{-} obtained above at the ratio of $[PI^{-}]/[PS_{\beta\alpha\beta}] = 3/1$ in THF at 195 K for 5 days. After being quenched with methanol, the final polymer was precipitated into an excess amount of methanol.

Roughly 1–5 g of PS_{α} and PS_{β} were used for the synthesis of $PS_{\beta\alpha\beta}$, respectively, and approximately 1–2 g of $PS_{\beta\alpha\beta}$ and 3–6 g of living PI were used for the synthesis of A_3B_2 type graft copolymer.

Fractionation

In the course of reaction preparing $PS_{\beta\alpha\beta}$, PS_{β} was still included. $PS_{\beta\alpha\beta}$ was isolated by GPC-fractionation at room temperature using fully automatic instrument of Tosoh Ltd. type HLC-837 equipped with a set of columns, two G4000H6 and one G5000H6 of Tosoh Ltd., all of them are 600 mm in length, 21.5 mm i.d. Isolation of the graft copolymer from the mixture of the coupling reaction was carried out with the same instrument. All runs for GPC-fractionation were made with chloroform as eluent. The concentration of the polymer solution was *ca.* 1.0 (w/v)%. In the experiments, roughly 3–5 g of coupling mixtures were GPC-fractionated to give approximately 1–2 g of fractionated $PS_{\beta\alpha\beta}$s and A_3B_2 type graft copolymers.

Molecular Characterization

Number-average molecular weights, M_ns, were determined by vapor pressure osmometry in benzene at 308 K with Corona type 117 instrument, and membrane osmometry in toluene at 303 K with a Hewlett-Packard type 502. Molecular weight heterogeneities, M_w/M_n, were obtained by GPC with a set of three GMHXL columns of Tosoh Ltd. with 300 mm length and with 7.8 mm i.d. ^{1}H NMR spectra were tested with a JEOL EX-400 FT-NMR spectrometer at 399.65 MHz. Chemical shift was referred to chloroform in chloroform-*d*.

Morphological Observation

Films used for morphological observation were cast from *ca.* 5% benzene solutions of samples for a few days under nitrogen gas atmosphere. The cast films were dried for 6 h and annealed at 423 K for a week in a vacuum oven. The films were cut into ultrathin sections (50–80 nm thick) by an ultramicrotome, Reichert Ultracut N equipped with a clyosectioning system, Reichert FC-4, with a Diatome diamond knife at a sample temperature of 163 K and a knife temperature of 173 K. The sections were stained with osmium tetroxide vapor at 298 K for 3 h. The morphology of the sections was observed by a JEOL transmission electron microscope JEM-2000FX-II operated at an accelerating voltage of 120 kV.

Small-angle X-Ray scattering (SAXS) was carried out using a M18XHF[22] of MAC Science Co. having Kratky camera system with a copper target X-Ray source. The monochromated Cu-K_{α} line with λ of 0.154 nm was used for the measurements. A scintillation counter and a step-scan goniometer were also provided. Operating conditions were 40 kV/200 mA or 43 kV/390 mA.

RESULTS AND DISCUSSION

Preparation and Characterization of Backbone Polymers

Figure 2 shows a GPC diagram of synthetic steps for a backbone polymer $PS_{\beta\alpha\beta}$. When styrene was added to lithium naphthalenide dissolved in THF at 195 K, the solution showed the characteristic yellow color of polystyryllithium. The color remained unchanged for 1 h at 195 K but immediately changed to dark red upon addition of DPE, followed by disappearance in color upon addition of **I** at room temperature. Molecular weight distribution of the telechelic polymer, PS_{α}, is narrow enough as shown in Figure 2a and the yields of

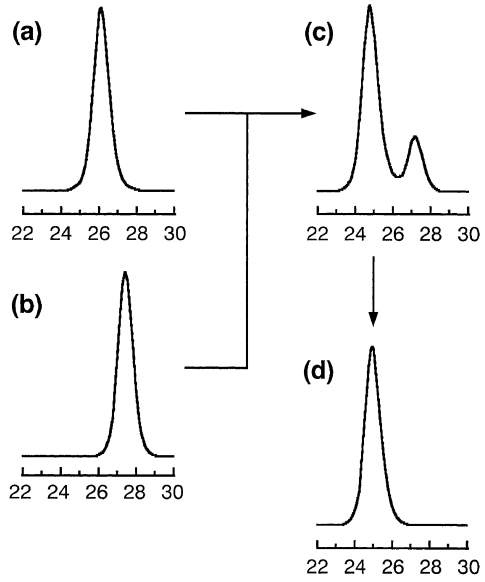


Figure 2. GPC chromatograms showing the synthesis of the backbone polymer, B5; (a) PS_{α}, (b) PS_{β}, (c) product of the coupling reaction among one PS_{α} chain and two PS_{β} chains and (d) the fractionated backbone polymer, $PS_{\beta\alpha\beta}$.

Table I. Molecular characteristics of backbone polymers

Sample	PS_α		PS_β		Backbone		R^b
	$10^{-4}M_n$[a]	M_w/M_n[a]	$10^{-4}M_n$[a]	M_w/M_n[a]	$10^{-4}M_n$[a]	M_w/M_n[a]	
B1	–	–	5.36	1.07	10.4	1.09	0
B2	1.33	1.08	4.11	1.07	9.66	1.09	0.14
B3	1.93	1.08	3.89	1.08	10.3	1.08	0.20
B4	3.27	1.08	3.03	1.07	9.73	1.07	0.35
B5	5.28	1.09	2.48	1.07	9.99	1.10	0.52
B6	6.57	1.10	1.60	1.06	10.0	1.09	0.67
B7	10.8	1.08	–	–	10.8	1.08	1.00

[a]Determined by GPC. [b]$R = M_n(PS_\alpha)/M_n(\text{Backbone})$.

all the PS_αs are 100% within experimental errors. M_ns of PS_αs are close to the kinetic molecular weight, M_ks, which are calculated from the polymer yield, the molar ratio of styrene monomer to lithium naphthalenide. ^{1}H NMR spectrum of PS_αs showed a signal at 5.4 ppm corresponding to vinyl protons in DPE unit and it is found that the M_n of PS_α determined by GPC agree well with those calculated from the intensity ratio of phenyl protons and vinyl protons in DPE units on both chain ends in the ^{1}H NMR spectrum. This fact implys quantitative end-capping with DPE followed by introduction of **I** onto bifunctional polystyryllithium.

In coupling of telechelic PS_αs with two living PS_βs, about five-fold molar amount of the latter relative to the former were added, since the desired backbone polymers cannot be obtained quantitatively if the amounts of living PS_βs are smaller than the double molar amounts of PS_αs. The residual, unreacted living PS_βs were end-capped with DPE, the **I** was added at 195 K, and then temperature of the solution was raised to room temperature. GPC chromatograms of the coupling products showed the bimodal peaks in Figure 2c. The products were fractionated into two fractions, and the higher molecular weight fractions were collected. A GPC chromatogram for the polymer is shown in Figure 2d. In the chromatogram in Figure 2d, there are no peaks or shoulders corresponding to PS_α and PS_β in Figures 2a and 2b and gives reasonably narrow molecular weight distribution. M_n of the polymer, 99.9 K, agrees well with $M_n(PS_\alpha)$ plus double of $M_n(PS_\beta)$, *i.e.*, 102 K. Hence the isolation of a backbone polymer from as-coupled polymer mixture was achieved by fractional GPC.

Table I lists the molecular characteristics of seven backbone polymers. The seven polymers had nearly the same chain length at 100 K as designed, and that they have fairly narrow molecular weight distributions ($M_w/M_n \leqq 1.10$), but different functional sites. To define the locations, the following parameter R is introduced.

$$R = \frac{M_n(PS_\alpha)}{M_n(\text{Backbone})}$$

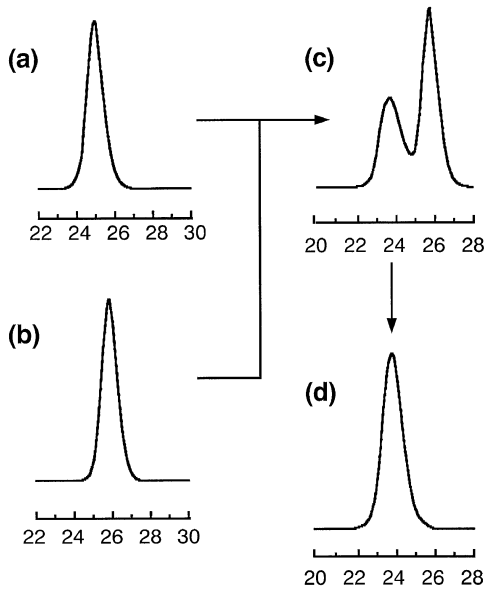


Figure 3. GPC chromatograms showing the synthesis of the graft copolymer, B5-G40; (a) $PS_{\beta\alpha\beta}$, (b) PI, (c) product of the coupling reaction between $PS_{\beta\alpha\beta}$ and two PI chains, and (d) the fractionated graft copolymer, B5-G40.

Preparation and Characterization of A_3B_2 Type Graft Copolymers

Figure 3 shows a GPC diagram of synthetic steps for a graft copolymer of the A_3B_2 type. After the second coupling reaction between a $PS_{\beta\alpha\beta}$ and a polyisoprenyllithium, the GPC peak at the elution volume of 25.0 mL corresponding to $PS_{\beta\alpha\beta}$ shown in Figure 3a disappeared and a new peak appeared at 23.5 mL leaving the peak at 26.0 mL polyisoprenyllithium unchanged which was added excessively as shown in Figure 3c. The polymers were fractionated again into two fractions and the higher molecular weight fraction was collected. The final polymers showed unimodal and fairly narrow molecular weight distributions as shown in Figure 3d. M_n of the final product, 176 K, is very close to $M_n(PS_{\beta\alpha\beta})$ plus double of M_n(PI), 179 K. Volume fractions of the grafted polyisoprenes estimated from the ^{1}H NMR signal intensity ratio of vinyl to phenyl protons are all close to the values estimated on the basis of

Table II. Molecular characteristics of graft copolymers

Sample	Backbone	Pl-graft	Graft	Graft copolymer	R[c]	Φ_{Pl}[d]	D/nm[e]
		$10^{-4}M_n$[a]	$10^{-4}M_n$[a]	M_w/M_n[b]			
B1-G40	B1	3.96	19.9	1.09	0	0.50	56.8
B2-G38	B2	3.76	18.8	1.09	0.14	0.51	50.6
B3-G40	B3	3.96	17.5	1.13	0.20	0.44	47.6
B4-G40	B4	3.96	17.1	1.08	0.35	0.46	42.7
B5-G40	B5	3.96	17.6	1.10	0.52	0.46	50.8
B6-G40	B6	3.96	16.7	1.11	0.67	0.43	48.5
B7-G40	B7	3.96	18.3	1.09	1.00	0.44	52.9

[a]Determined by Osmometry. [b]Determined by GPC. [c]$R = M_n(PS_\alpha)/M_n$(Backbone). [d]Estimated from ^{1}H NMR. [e]Domain spacing calculated by $D = 2\pi/q_1$.

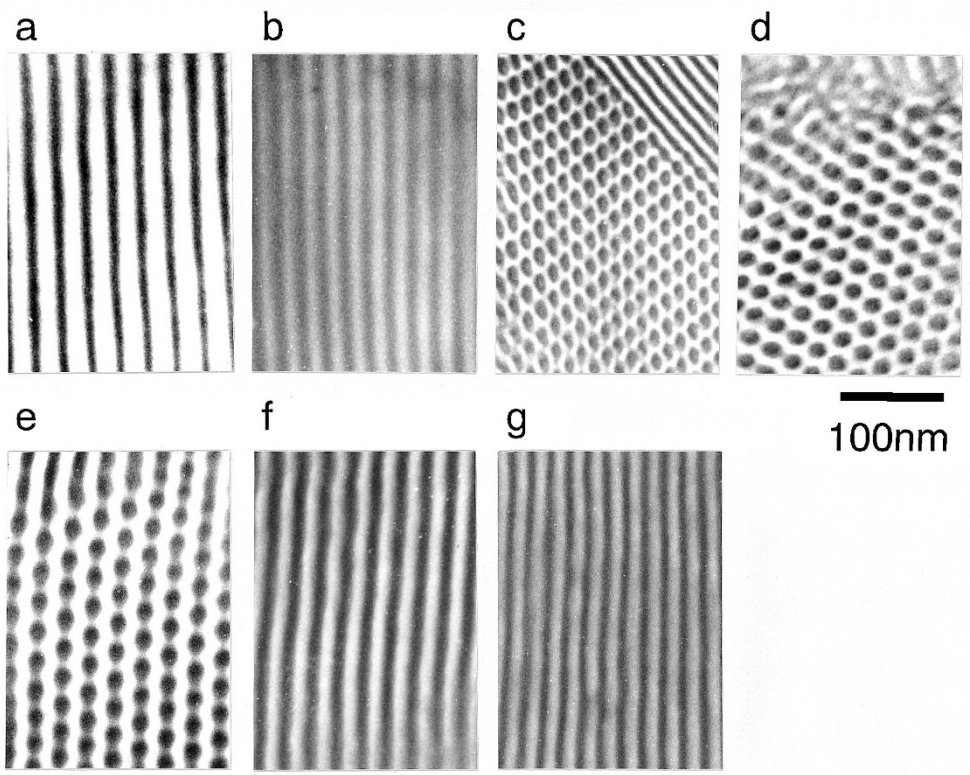


Figure 4. Electron micrographs of the graft copolymers: (a) B1-G40; (b) B2-G38; (c) B3-G40; (d) B4-G40; (e) B5-G40; (f) B6-G40; (g) B7-G40.

M_n values measured.

Molecular characteristics of the A_3B_2 type graft copolymers are listed in Table II. M_n of the seven graft copolymers agree well with stoichiometric ones, that is, $M_n(PS_{\beta\alpha\beta})$ plus double of M_n(PI) and they have relatively narrow molecular weight distributions ($M_w/M_n \leqq 1.13$), and almost the same molecular weights and compositions.

Thus we concluded that polymers in Table II obtained from the synthetic procedure adopted in this study are graft copolymers of the A_3B_2 type with different junction points, but with the same backbone and graft chain lengths as designed.

The Dependence of Branching Positions on Morphology

Figure 4 shows micro phase-separated structures of A_3B_2 type graft copolymers. Figures 4a, b, f, and g are TEM images from samples B1-G40 ($R = 0$), B2-G38 ($R = 0.14$), B6-G40 ($R = 0.67$), and B7-G40 ($R = 1.0$), respectively. These samples show alternating lamellar structures. Figures 4c, d, and e are TEM images of samples B3-G40 ($R = 0.20$), B4-G40 ($R = 0.35$), and B5-G40 ($R = 0.52$), respectively, which show hexagonally packed cylinders, polyisoprene in polystyrene matrix.

Figure 5 shows SAXS intensity profiles of 7 samples. The 4 curves for the samples B1-G40 ($R = 0$), B2-G38 ($R = 0.14$), B6-G40 ($R = 0.67$), and B7-G40 ($R = 1.0$) in Figure 5 shows multi-reflection peaks at the relative magnitudes q_n/q_1 of integer, where $q_n(=4\pi n \sin\theta/\lambda)$ is

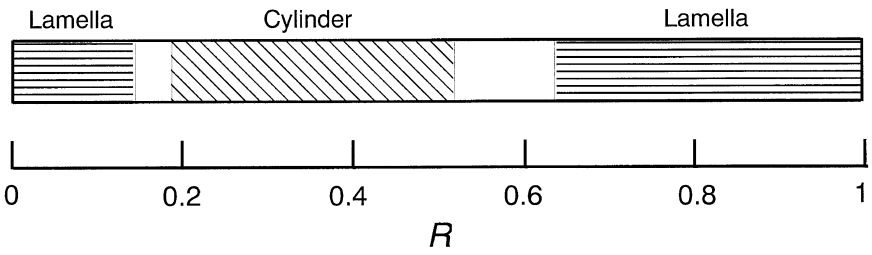


Figure 6. Variation in microdomain structure of graft copolymers as a function of positional parameter *R*.

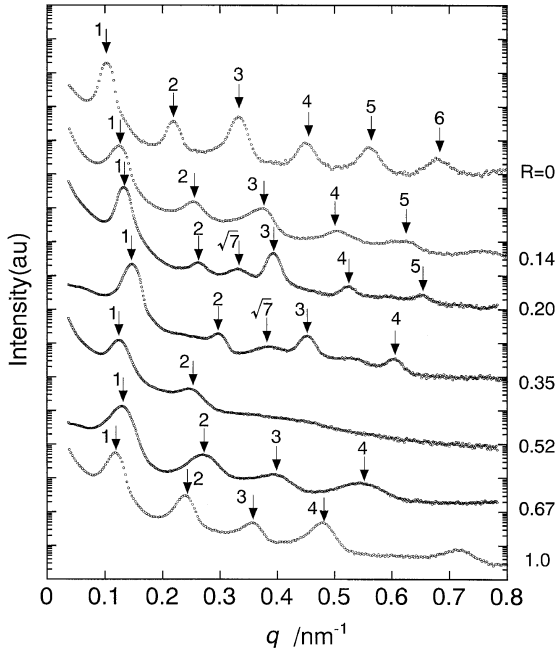


Figure 5. SAXS diffraction patterns of seven graft copolymers.

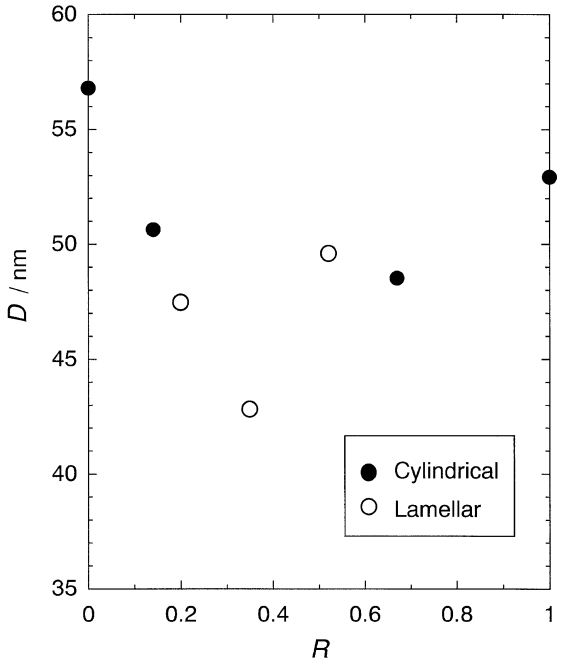


Figure 7. Domain spacings of graft copolymers with positional parameter *R*.

the magnitude of the scattering vector of the *n*-th order, λ is the wavelength of X-Ray and 2θ is the scattering angle, which indicates alternating lamellar structures. These findings are quite consistent with the results from TEM. The two curves for the samples B3-G40 (R = 0.20) and B4-G40 (R = 0.35) in Figure 5 show the multi-reflection peaks at the ratio q_n/q_1 of 1, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, and more, which indicates the arrangement of hexagonally packed cylinders in matrix, since the peak at q_n/q_1 of $\sqrt{3}$ should be surpressed because of the scattering form factor from the hexagonal cylinders whose volume fraction being around 0.45. The curve for the samples B5-G40 (R = 0.52) in Figure 5 shows relatively weak reflection peaks at 1 and 2(= $\sqrt{4}$) in terms of q_n/q_1. If this sample has an alternating lamellar structure, the third peak at $3q_1$ should be higher than the second one at $2q_1$ because of the form factor from lamellar structure with relative thickness of two phase of 0.45/0.55 which corresponds to the volume fraction of this sample. Therefore the morphology of this sample should not be lamellar but cylindrical. The disappearance of peaks at $\sqrt{7}$, $\sqrt{9}$, and higher could be attributed to low orientation of cylinders for this sample. Thus all SAXS results agree well with those from TEM.

In Figure 6, variation of morphology is given as a function of R. In this diagram, it is quite reasonable that alternating lamellar structures appear on both ends at R = 0 and R = 1.0, where polymers are actually an A_2B_2 type star-shaped copolymer and a BAB type triblock copolymer, respectively, who both should show the alternating lamellar structures. The alternating lamellar structure also appears when R equals to 0.14. This can be easily understood since the molecular architecture of sample B2-G40 (R = 0.14) is close to that of the A_2B_2 type star-shaped copolymer. Sample B6-G40 (R = 0.67) also gives lamellar structure, which means that this copolymer is as a family of the BAB type triblock copolymer.

The cylindrical structures of polyisoprene appear in the range of $0.20 \leqq R \leqq 0.52$, that may be due to the asymmetric connection effect in graft copolymers, as described above. This indicates that the morphology of graft copolymers of the A_3B_2 type changes with branching positions, even though the composition ratio of components is constant.

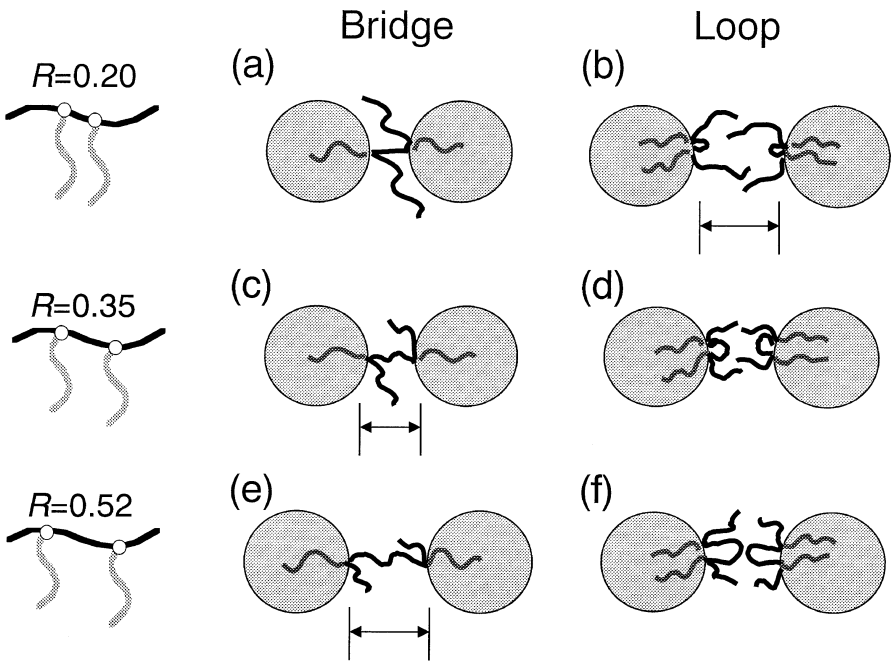


Figure 8. Schematic illustrations of two chain conformations of graft copolymers of A_3B_2 type with different *R*.

Domain spacing D ($=2\pi/q_1$) of graft copolymers is listed in Table II and plotted against positional parameter R in Figure 7. D has a minimum at $R = 0.35$. One might be able to explain the shortest domain spacing at $R = 0.35$ using Figure 8. Middle blocks of backbones in A_3B_2 type graft copolymers may have two kinds of conformations, a bridge and loop as shown in Figure 8. First for a graft copolymer molecule with R of 0.20, the chain length of a middle block in a backbone is one fourth the total of two end blocks. If a molecule has the bridge conformation preferentially, the short middle block chain might keep the domain spacing shorter, and hence, both end block chains in backbones cannot be packed within the narrow matrix region as is shown in Figure 8a. If the molecule has a loop conformation, no chains are subjected to strain. Therefore, the molecules with R of 0.20 might choose the loop conformation. Consequently, the domain spacing of the molecule with R of 0.20 is dominated by the longer block chain. That is the end block chains in backbones as shown in Figure 8b. Secondly for a graft copolymer molecule with R of 0.35, since the chain length of a middle block and both end blocks are almost the same, a molecule can probably take either conformation. Domain spacing of this molecule can be determined by chains with two conformations. The bridge one may give minus contribution while the loop one may widen the spacing. Thirdly for the graft copolymer molecules with R of 0.52, the chain length of a middle block is almost double that of an end block, so the molecules can adopt both conformations again. In either conformation, the domain spacing must be controlled by the longest middle block chain, therefore, D for this molecule must be considered longer than that of a molecule with R of 0.35. Summarizing this consideration, the domain spacing D for three molecules with different R value might be the following order,

$$D_{(R=0.35)} < D_{(R=0.52)} < D_{(R=0.20)}$$

Domain spacing of the A_3B_2 type graft copolymer with R of 0.67 is shorter than that with R of 1.0 at the right end in Figure 7. This may be easily explained by the illustration in Figure 9. Comparing both chain conformations in lamellar structures, domain thickness of polystyrene should be predominantly determined by the chain length of middle block (PS_α) in backbone. The middle block chain length of graft copolymer molecule with R of 0.67 is apparently shorter than that with R of 1.0, this causes polystyrene domain thickness of the former to be thinner than that of latter, since the volume fraction of two component are almost the same, thickness of PI phase of the former is also thinner than the latter. Therefore junction point density of the former could be lower than that of the latter considering the primary requirement of constant segment density in bulk. Consequently the total domain spacing of a graft copolymer molecule with R of 0.67 could be shorter than that of a regular block copolymer.

Domain spacings of the A_3B_2 type graft copolymers with R of 0.14 is shorter than those with R of 0 at the left end in Figure 7. This difference may be explained as in the above paragraph and shown in Figure 10. For polystyrene chains, effective chain length in a graft copolymer is shorter than that of a star-branched

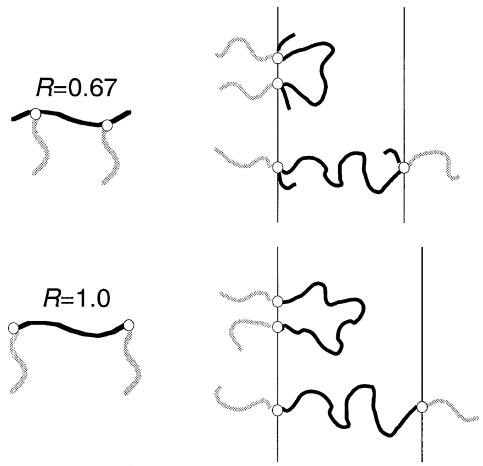


Figure 9. Comparison of chain conformations of two graft copolymers of A_3B_2 type with *R* of 0.67 and 1.0.

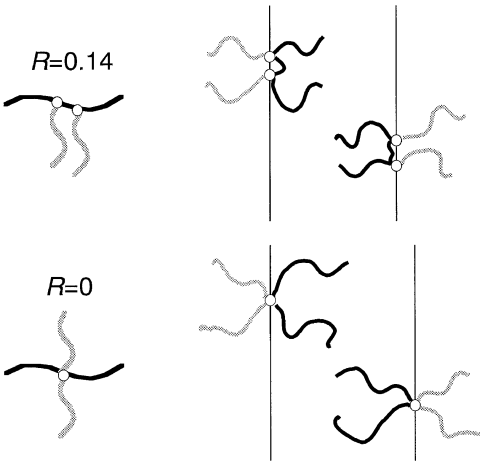


Figure 10. Comparison of chain conformations of two graft copolymers of A_3B_2 type with *R* of 0.14 and 0.

A_2B_2 block copolymer as shown in Figure 10. An end block chain length of a graft copolymer molecule with *R* of 0.14 is apparently shorter than that with *R* of 0, threrfore domain thickness of polystyrene phase with *R* of 0.14 should be thinner than that with *R* of 1.0. Junction point density with *R* of 0.14 should be lower than that of *R* of 0, and both polyisoprene phase have almost the same volume. Therefore the domain thickness of polyisoprene phase with *R* of 0.14 should be thinner than that with *R* of 0. Consequently the total domain spacings of a graft copolymer molecule with *R* of 0.14 could be shorter than that of a molecule with *R* of 0, *i.e.*, star-branched A_2B_2 chain.

From preparation and morphological studies on graft copolymers of the A_3B_2 type, following conclusions can be derived. Graft copolymers of the A_3B_2 type with well-defined molecular structure were successfully prepared as designed by way of new preparation method using DPE group as a reaction controller. Graft copolymers form cylindrical structures, not alternating lamellar structures, even though the volume fraction of graft chains, Φ_{PI}, is about 0.5. The cross-over from block copolymer to graft one on the morphological behavior was observed in between 0.67 and 0.52 in terms of positional parameter, *R*. The lamellar domain spacings of the A_3B_2 type graft copolymers with *R* of 0.14 and 0.67 were shorter than those with *R* of 0 and 1.0, respectively.

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