

Synthesis and Blend Morphology of BA/BC-Type Binary Graft Copolymers Composed of Polyelectrolyte Trunks

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SYNOPSIS

Poly(α -methylstyrene) (PMS) macromonomer having one vinylbenzyl group per polymer chain was prepared by the couplings of living PMS with *p*-chloromethylstyrene (CMS). Subsequently, well-defined poly[acrylic acid (AA)-*g*- α -methylstyrene (MS)] and poly[4-vinylpyridine (4VP)-*g*-MS] graft copolymers composed of polyelectrolyte trunks were prepared by radical copolymerization of PMS macromonomer with AA and 4VP monomers, respectively. Binary poly(AA-*g*-MS)/poly(4VP-*g*-MS) or poly[AA·triethyl amine (Et₃N) salt-*g*-MS]/poly(4VP-*g*-MS) graft copolymer blend films were cast from a benzene/methanol mixture. The morphological results of binary graft copolymer blends are discussed with respect to three-phase separated structures.

INTRODUCTION

Since Milkovich et al.¹⁻³ demonstrated the syntheses and applications of a variety of macromonomers, it has been established that the macromonomer technique is one of the best for the preparation of well-defined graft copolymers. Asami et al.⁴ reported that polystyrene (PS) macromonomer having one vinylbenzyl group per polymer chain was prepared by a coupling reaction of living PS with *p*-chloromethylstyrene (CMS) such as electrophiles.

Block and graft copolymers composed of incompatible block segments generally form a microdomain structure in the solid state as a consequence of microphase separation of the constituent block chains. The morphology of diene-containing block copolymers has been most extensively studied and found to depend, according to Molau's rule,⁵ on the volume fraction of the phases. Mesomorphic structure of three-phase systems has also been studied for ABC-type triblock copolymers.⁶⁻⁸

Blending of block and graft copolymers with other homopolymers is an industrially useful technique for the production of new polymeric materials. In fundamental studies⁹⁻¹² of polymer blends of the AB-

type block copolymer/poly A/poly B, it has been shown that a given homopolymer can be solubilized in the microdomains formed by the AB-type block copolymer up to a certain amount. The miscibility of homopolymers in the domains is possible as long as the molecular weight of the homopolymers does not greatly exceed that of the block sequence of composition.¹¹

Most studies of polymeric surfactants, typically of block copolymer, focus on single-component systems. The problem of mesomorphic structures of binary BA/BC-type graft copolymer blend composed of polyelectrolyte trunks is very interesting, because interactions between the oppositely charged segments lead to poly-ion complex formation. If we can fabricate the three-phase separated microdomains from binary graft copolymer blends, it is possible to pass the complicated synthesis process on the ABC-type triblock copolymers. Moreover, the polymeric materials in which the oppositely charged phases are separated with the insulator phase can be applied for charge mosaic membranes¹³ and thermal-reversible ion-exchange resins.¹⁴

In this article, poly(α -methylstyrene) (PMS) macromonomer having one vinylbenzyl group per polymer chain was prepared by the couplings of living PMS with CMS. Subsequently, well-defined poly[acrylic acid (AA)-*g*- α -methylstyrene MS] and poly[4-vinylpyridine (4VP)-*g*-MS] graft copoly-

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mers were prepared by radical copolymerization with AA and 4VP monomers, respectively. The morphological behavior of binary graft copolymer blends was investigated with respect to three-phase separated structures.

EXPERIMENTAL

Macromonomer Synthesis and Characterization

The MS monomer was first dried over a mixture of calcium hydride–lithium aluminum hydride and then treated with tetrahydrofuran (THF) solution of *n*-butyllithium (*n*-BuLi) in vacuum. The CMS was dried over a mixture of calcium hydride–lithium aluminum hydride and then treated with THF solution of sodium naphthalene in vacuum. The purified THF was distilled from THF solution of sodium MS tetramer anion. Living PMSs were prepared by the usual anionic polymerization of MS using *n*-BuLi as an initiator in THF at -78°C . An aliquot was taken out to recover the polymer for characterization, and living ends were terminated with THF solution of CMS at -78°C for 2 h. Polymerization and termination were carried out in a sealed glass apparatus, and other techniques have been described earlier.¹⁵ The obtained PMS macromonomer was purified three times by reprecipitation from THF into methanol.

The number-average molecular weight (\bar{M}_n) of the PMS macromonomers was determined by vapor pressure osmometry on a Corona NA 117 vapor pressure osmometer in benzene. The content of terminal vinylbenzyl groups was determined by the area ratio of refractive index (RI) and UV (292 nm) intensities in a gel permeation chromatography (GPC) chart on a Tosoh high-speed liquid chromatography HLC-802A, with chloroform as eluent at 38°C , a TSK gel G4000HXL and G2500 HXL columns, and a flow rate of 1.0 mL/min (by a calibration curve constructed from a mixture of the PMS prepolymer and *p*-MS). The polydispersity (\bar{M}_w/\bar{M}_n) was determined from GPC distribution functions improved by the reshaping method¹⁶ with an NEC personal computer PC-8801.

Copolymerization

The radical copolymerization of vinylbenzyl-terminated PMS macromonomer with AA was carried out in benzene/THF (5/1 : v/v) mixture at 60°C initiated by 2,2'-azobisisobutyronitrile (AIBN) using diphenyl disulfide as a chain transfer reagent in

a sealed ampule under high vacuum. Polymerization was stopped by introducing the resulting viscous solution into an excess of *n*-hexane. Homo(PMS) and homo[poly(acrylic acid) (PAA)] were extracted twice with cyclohexane and methanol, respectively, for 16 h.

On the other hand, the radical copolymerization of vinylbenzyl-terminated PMS macromonomer with 4VP was carried out in a benzene/ethanol (3/1 : v/v) mixture at 60°C initiated by AIBN using 4,4'-dipyridyl disulfide as a chain transfer reagent. Polymerization was stopped by introducing the resulting solution into an excess of *n*-hexane. Homo(PMS) and homo[poly(4-vinylpyridine) (P4VP)] were extracted twice with cyclohexane and methanol, respectively.

Poly(AA·Et₃N salt-*g*-MS) was converted with the reaction of poly(AA-*g*-MS) with an excess of Et₃N in a benzene/THF mixture. The resulting solution was introduced into an excess of *n*-hexane.

The formation of graft copolymers was recognized by GPC with chloroform as eluent and IR spectra (Hitachi grating infrared spectrometer 285). The \bar{M}_n of both graft copolymers were obtained with a GPC that had been calibrated with PS standards. The composition ratio of PAA to PMS components was measured by IR spectra by the absorptions at 700 cm^{-1} (aromatic ring) and 1720 cm^{-1} (carboxyl group). Similarly, the composition ratio of P4VP to PMS components was also measured in IR by the absorptions at 700 cm^{-1} (aromatic ring) and 820 cm^{-1} (pyridine ring).

Turbidimetric Measurements

To determine the polymer concentration at the core-shell-type micelle formation of graft copolymers, the turbidimetric measurement of poly(AA-*g*-MS), poly(AA·Et₃N salt-*g*-MS), and poly(4VP-*g*-MS) graft copolymers was carried out in a benzene/methanol (9/1 : v/v) mixture at the wave length of 500 nm (measurement temperature, 25°C ; Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer).

Morphology of Graft Copolymers and Binary Copolymer Blends

Ultrathin film specimens of poly(AA-*g*-MS), poly(AA·Et₃N salt-*g*-MS), and poly(4VP-*g*-MS) graft copolymers were prepared for electron microscopy by placing a drop of a 1.0 wt % benzene/methanol (9/1 : v/v) mixture on a microscopy mesh coated with a carbon film and evaporating the sol-

vent as gradually as possible at room temperature. The poly(AA-*g*-MS) and poly(4VP-*g*-MS) graft copolymer specimens were exposed to the aqueous solution of cesium hydroxide (CsOH) and the vapor of methyl iodide (MeI), respectively. The CsOH and MeI stained selectively PAA and P4VP phases, respectively.

In general, the interactions between the oppositely charged segments lead to poly-ion complex formation. In fact, the benzene/methanol mixture of poly(AA-*g*-MS)/poly(4VP-*g*-MS) binary copolymer blends formed the poly-ion complex. We prepared separately a 2.0 wt % benzene/methanol mixture of poly(AA-*g*-MS) or poly(4VP-*g*-MS) graft copolymers. Next, both solutions were mixed with equal volume. This binary BA/BC-type graft copolymer blend solution did not form a precipitation of poly-ion complex. The thin film specimens of binary BA/BC-type graft copolymer blends were made by placing 1 drop of 2.0 wt % benzene/methanol mixture prepared above, on top of the carbon films. These specimens exposed to the vapor of MeI and subsequently to the aqueous solution of CsOH. These specimens were washed with a small amount of fresh water.

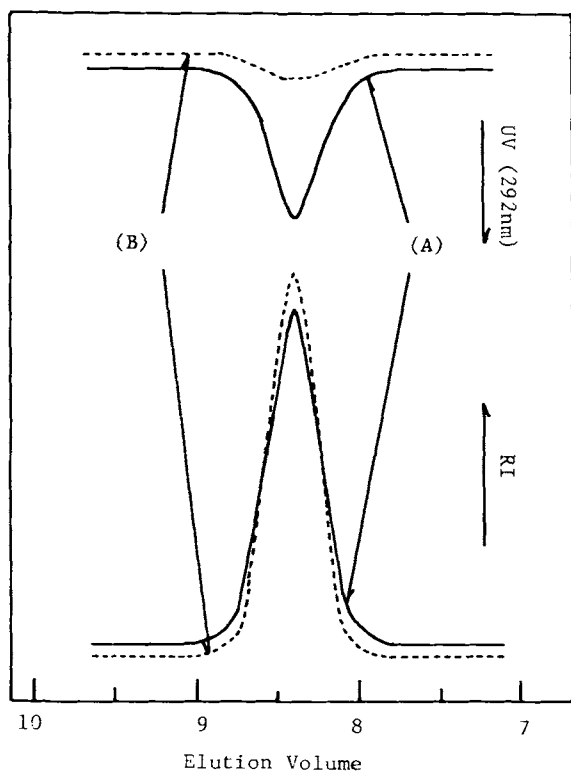


Figure 1 GPC profiles of macromonomer PMS2 and its precursor prepared by anionic polymerization: (A) macromonomer PMS2; (B) PMS precursor.

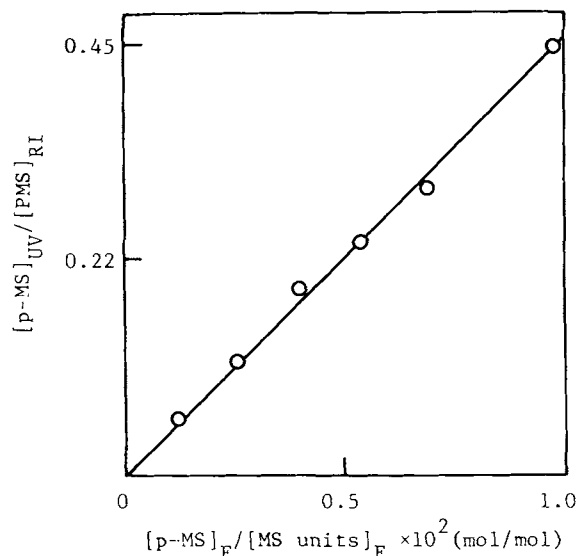


Figure 2 Calibration curve constructed from a mixture of *p*-methylstyrene (*p*-MS) and PMS prepolymer by using GPC double detectors (RI and UV at 292 nm): $[p\text{-MS}]_{\text{UV}}$, area of GPC distribution of *p*-MS in a UV monitor at 292 nm; $[PMS]_{\text{RI}}$, area of GPC distribution of PMS prepolymer in a RI monitor; $[p\text{-MS}]_{\text{F}}$, feed (mol) of *p*-MS in a mixture; $[MS \text{ units}]_{\text{F}}$, feed (mol) of MS units in a mixture.

The benzene/methanol mixture of poly(AA·Et₃N-*g*-MS)/poly(4VP-*g*-MS) binary graft copolymer blend also did not form a precipitation of poly-ion complex. The thin-film specimens of poly(AA·Et₃N-*g*-MS)/poly(4VP-*g*-MS) binary blends were also made by placing 1 drop of a 2.0 wt % benzene/methanol (9/1 v/v) mixture, on top of the carbon films. These specimens were exposed to the aqueous solution of CsOH, washed with a small amount of fresh water, and subsequently exposed to the vapor of osmium tetroxide (OsO₄). The OsO₄ stained selectively P4VP phases. Morphological results were obtained on a Hitachi H-600A transmission electron microscope (TEM).

RESULTS AND DISCUSSION

Macromonomer Synthesis

Figure 1 shows typical sets of GPC profiles of macromonomer PMS2 (A) and PMS precursor. The molecular weight distribution of this macromonomer determined by GPC is 1.02. A dotted line shown in Figure 1 denotes GPC distribution of PMS precursor (B) terminated with methanol. The wave length of the UV detector is set at 292 nm of the characteristic absorption of vinylbenzyl groups. The GPC elution

Table I Characteristics of PMS Macromonomers

Macromonomer Code	$10^{-4} \bar{M}_n^a$	\bar{M}_w/\bar{M}_n^b	Vinylbenzyl Groups ^c (Per Polymer)
PMS1	0.9	1.17	1.03
PMS2	3.4	1.02	0.92

^a Determined by vapor pressure osmometer.

^b Determined by GPC.

^c Determined by GPC double detectors.

pattern of macromonomer PMS2 (A) is identical with that of the PMS precursor (B) in the RI monitor. However, it is found from the UV monitor that the intensity of UV absorption for PMS2 is larger than that of the PMS precursor. Figure 2 shows a calibration curve constructed from a mixture of the PMS prepolymer and *p*-MS as the model compound. The end-group functionality of macromonomer PMS2 is determined to be 0.92 by using the above calibrations. The characteristics of PMS macromonomers are listed in Table I.

Copolymerization

Table II lists the results for syntheses of poly(AA-*g*-MS) and poly(4VP-*g*-MS) graft copolymers. The conversions of AA and 4VP monomers are about 80–100% in both copolymerizations. Typical IR spectra of each extract by solvents and unextract for GAS are shown in Figure 3. The extract by methanol is recognized from IR spectrum to be homo(PAA). However, not only the aromatic ring absorptions at 1600 and 700 cm^{-1} but a small absorption of the carbonyl group at 1720 cm^{-1} appear in the IR spectrum of extract by cyclohexane. Therefore, the extract of cyclohexane is a mixture of homo (PMS) and a small amount of poly(AA-*g*-

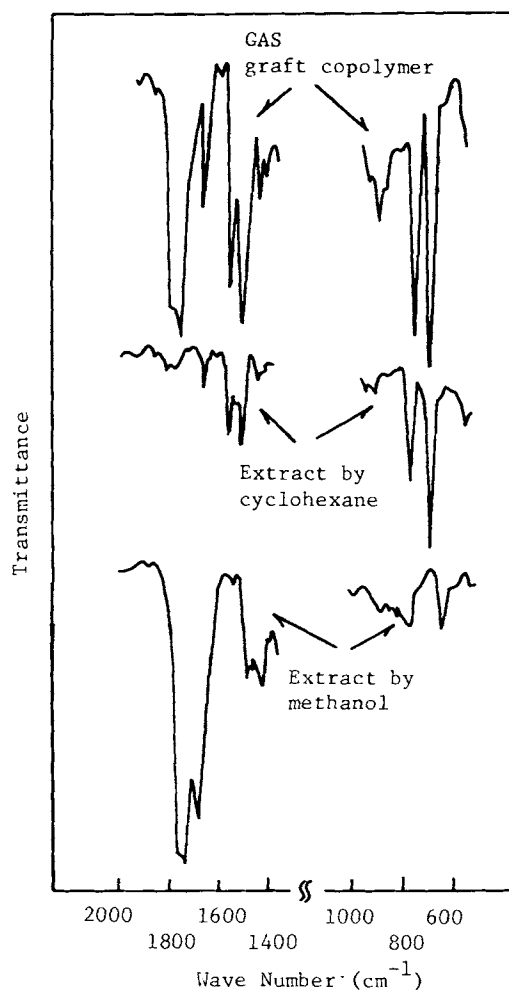


Figure 3 IR spectra of unextract (graft copolymer GAS) and extract by solvents (cyclohexane and methanol).

MS) graft copolymer. As a matter of course, absorptions both of aromatic ring and carbonyl group are maintained in the spectrum of the unextract (graft copolymer GAS). Figure 4 shows GPC profiles

Table II Results for Syntheses of Poly(AA-*g*-MS) and Poly(4VP-*g*-MS) Graft Copolymers^a

Expt No.	PMS Macro-monomer		AA (4VP) (mL)	Diphenyl Disulfide (4,4'-dipyridyl Disulfide) (g)	Yield	Graft Copolymer		
	Code	(g)				$10^{-4} \cdot \bar{M}_n^b$	PMS ^c (Mol %)	Branch Number (Per Polymer)
GAS	PMS2	4.0	4	0.4	2.8	5.9	59.4	1.2
GVS	PMS1	3.1	(6)	(0.1)	2.3	1.2	70.2	1.0

^a Poly(AA-*g*-MS) (GAS), copolymerized in benzene/THF (5/1 : v/v) mixture at 60°C initiated by AIBN (90 mg); poly(4VP-*g*-MS) (GVS), copolymerized in benzene/ethanol (3/1 : v/v) mixture at 60°C initiated by AIBN (40 mg).

^b Determined by GPC.

^c Determined by IR spectra.

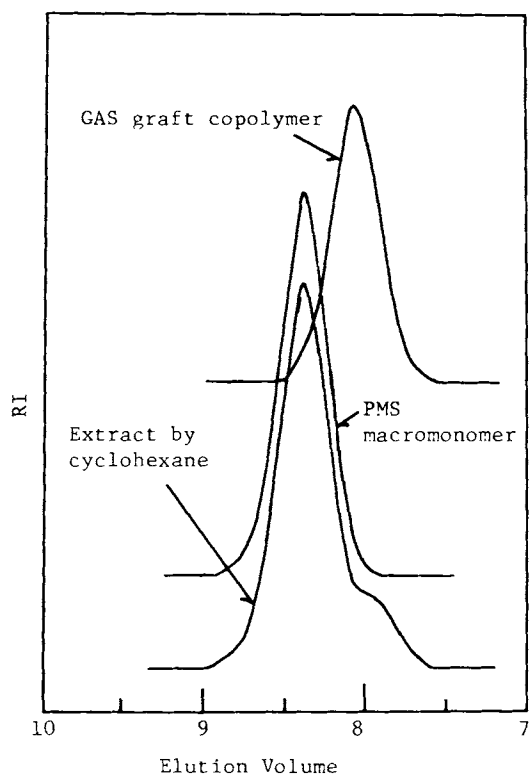


Figure 4 GPC profiles of graft copolymer GAS, extract by cyclohexane, and macromonomer PMS.

of graft copolymer GAS and the extract by cyclohexane with chloroform as eluent. In the RI chart, the extract by cyclohexane shows a bimodal pattern. The GPC distribution in the side of low molecular weight is identical with that of macromonomer PMS2. On the other hand, the elution peak count of GAS graft copolymer shifts to the side of high molecular weight compared with that of PMS macromonomer. Also, the GPC distribution of extract by cyclohexane on the side of high molecular weight is identical with that of poly(AA-*g*-MS) graft copolymer. The results of GPC analysis support those of the IR spectra shown in Figure 3.

The copolymerization result of poly(4VP-*g*-MS) graft copolymer (GVS) is also listed in Table II. The results of the solvent-extract for copolymerization products are almost similar to those of poly(AA-*g*-MS) graft copolymer. The extract by methanol is recognized from the IR spectrum to be homo(P4VP). The extract of cyclohexane is a mixture of homo(PMS) and a small amount of poly(4VP-*g*-MS) graft copolymer. The branch number and composition of both graft copolymers are about one per polymer molecule and in the range of PMS 60–70 mol %, respectively.

Micelle Formation of Graft Copolymers

Figure 5 shows typical turbidity curves of poly(AA-*g*-MS), poly(AA·Et₃N salt-*g*-MS) (GAS-E), and poly(4VP-*g*-MS) graft copolymers in benzene/methanol (9/1 : v/v) mixture, varying the polymer concentration. Each sample shows the maximum peak in turbidity curves at the range of 1.8–2.0 wt % of polymer concentration due to the micelle formation. These polymer concentrations correspond to the critical micelle concentration (CMC) of graft copolymers. The CMC of GAS-E shifts to the side of low polymer concentration compared with that of GAS. The GAS is soluble in the solvent composition of methanol fraction 0.1 but insoluble in the benzene/methanol mixture of methanol fraction more than 0.1. However, the GAS-E is soluble in the solvent composition of methanol fraction 0.1–0.3. Benzene seems to work as a relatively compatible solvent for PAA·Et₃N compared with that for PAA segments.

Morphology of Graft Copolymers and Binary Copolymer Blends

Figure 6(a), (b), and (c) show typical TEM micrographs of poly(AA-*g*-MS) : GAS; poly(AA·

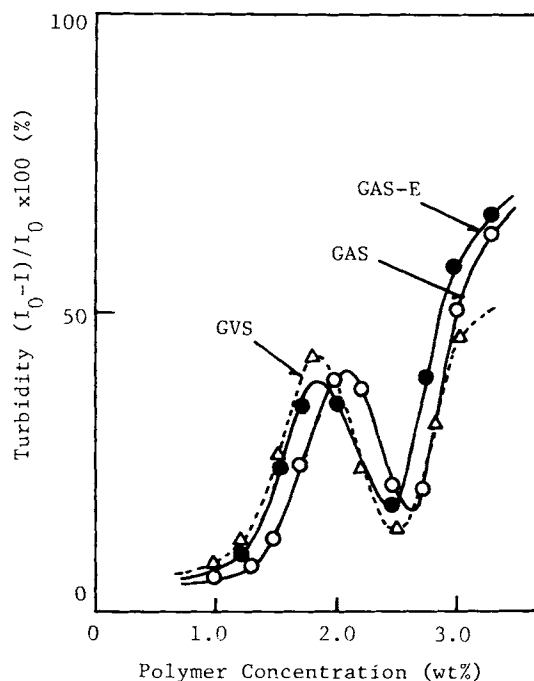
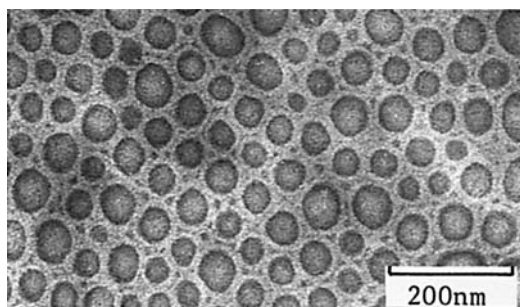
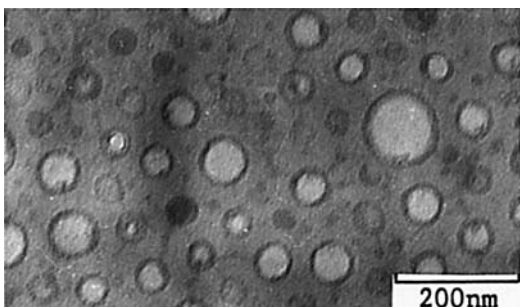


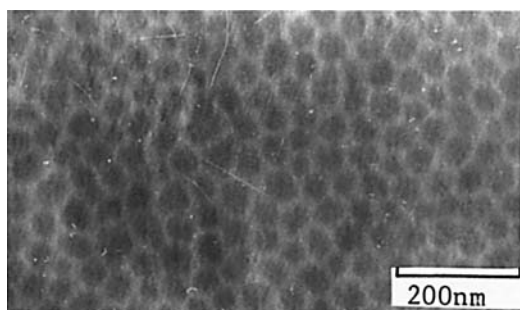
Figure 5 Turbidity curves of poly(AA-*g*-MS) (GAS), poly(AA·Et₃N-*g*-MS) (GAS-E), and poly(4VP-*g*-MS) (GVS) graft copolymers in benzene/methanol (9/1 : v/v) mixture, varying the polymer concentration.



(a) GAS



(b) GAS-E



(c) GVS

Figure 6 TEM micrographs of GAS, GAS-E, and GVS graft copolymers cast from benzene/methanol (9/1 : v/v) mixture: (a), GAS; (b), GAS-E; (c), GVS.

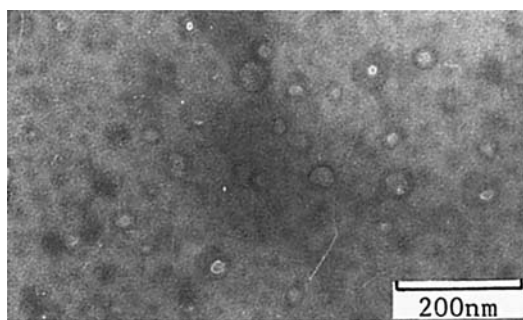
Et₃N-*g*-MS) : GAS-E; and poly(4VP-*g*-MS) : GVS graft copolymers; respectively, cast from a benzene/methanol (9/1 : v/v) mixture. The dark portions in Figure 6(a) and (b) are the selectively stained PAA and PAA·Et₃N phases, respectively. Both specimens show a microdomain structure of PAA or PAA·Et₃N spheres in a PMS matrix. The average radius of PAA spheres in the GAS specimen is 18 nm. The spherical size of PAA·Et₃N phases in the GAS-E specimen increases more than that of PAA phases in the GAS specimen. This fact seems to correspond to the difference of the CMCs observed in turbidities of GAS and GAS-E graft copolymers.

The dark portions shown in Figure 6(c) are the selectively stained P4VP phases. The GVS specimen (PMS 70.2 mol %) shows the domain structure of P4VP spheres in a PMS matrix.

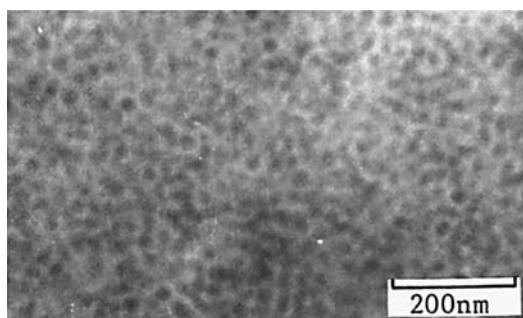
The benzene/methanol (9/1 : v/v) mixture of GAS/GVS binary graft copolymer blend prepared by a simultaneous mixing method forms a precipitation of the poly-ion complex. However, each 2.0 wt % benzene/methanol (9/1 : v/v) mixture of the GAS/GVS binary graft copolymer blend prepared by the stepwise mixing method does not form the precipitation of the poly-ion complex. It was made clear from the turbidimetric measurements that both GAS and GVS graft copolymers formed the core-shell-type micelles in this casting solvent at about 2.0 wt % of polymer concentration. Then, the core-shell-type micelles formed are considered to exhibit the molecular structure of PAA or P4VP spherical cores surrounding the PMS shells. Each micelle of these polymer microspheres moves like pseudolatex even in the state of the stepwise mixing. Figure 7 shows TEM micrographs of a GAS/GVS (1/1 : wt/wt) binary graft copolymer blend specimen cast from a 2.0 wt % benzene/methanol (9/1 : v/v) mixture using the stepwise mixing method. First, the thin-film specimen is stained with CsOH [micrograph 7(a)] or with MeI [micrograph 7(b)]. Each reagent can stain the PAA or P4VP phases only. On the other hand, the micrograph 7(c) shows the texture of a blend specimen stained with both CsOH and MeI. The dark spherical PAA and P4VP domains appearing in micrographs 7(a) and 7(b), respectively, are overlapped in the texture of micrograph 7(c). It can be concluded from these data that the PAA-P4VP poly-ion complex is formed during the solvent evaporation process. Probably, the core-shell type micelles constructed with PAA and P4VP cores interpenetrate with each other during the evaporation process.

Figure 8 shows TEM micrographs of a GAS-E/GVS (1/1 : wt/wt) binary graft copolymer blend specimen cast from a 2.0 wt % benzene/methanol (9/1 : v/v) mixture using the simultaneous mixing method. The thin-film specimen is stained with CsOH [micrograph 8(a)] or OsO₄ [micrograph 8(b)]. The number density of PAA·Et₃N spherical domains in micrograph 8(a) is about one-half of that in micrograph 6(b). On the other hand, the number density of P4VP spherical domains in micrograph 8(b) is similarly about one-half of that in micrograph 6(c). As a result, the three-phase separated structure (PAA·Et₃N and P4VP spheres dispersed in a PMS matrix) is formed in the texture of micrograph 8(c).

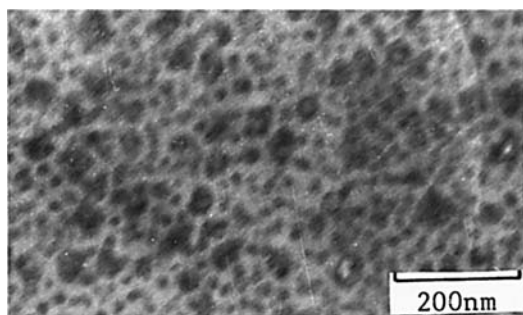
The possible molecular arrangements for the GAS-E/GVS binary graft copolymer blend within the domains in solution and solid are illustrated schematically in Figure 9. At the CMC (about 2.0 wt % of polymer concentration), each component segment of graft copolymer chains undergoes phase separation and aggregates into characteristic molecular micelles, i.e., the core-shell-type micelles with PAA·Et₃N or P4VP spherical cores are formed in selective solvent [Fig. 9(a)]. Each micelle of these polymer microspheres moves like pseudolatex in so-



(a) Stained with CsOH

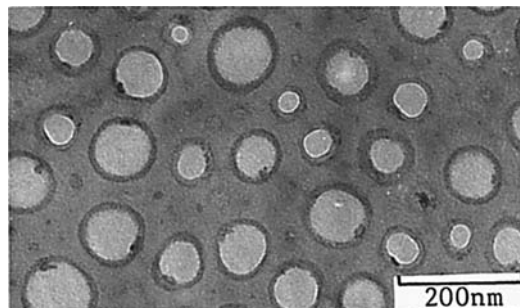


(b) Stained with MeI

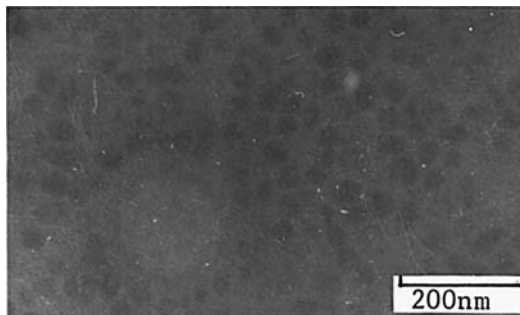


(c) Stained with CsOH and MeI

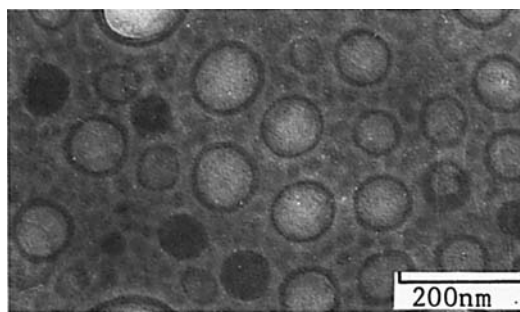
Figure 7 TEM micrographs of GAS/GVS (1/1 : wt/wt) binary graft copolymer blend cast from a 2.0 wt % benzene/methanol (9/1 : v/v) mixture using stepwise mixing method: (a) stained with CsOH; (b) stained with MeI; (c) stained with CsOH and subsequently with MeI.



(a) Stained with CsOH



(b) Stained with OsO₄



(c) Stained with CsOH and OsO₄

Figure 8 TEM micrographs of GAS-E/GVS (1/1 : wt/wt) binary graft copolymer blend cast from a 2.0 wt % benzene/methanol (9/1 : v/v) mixture using a simultaneous mixing method: (a) stained with CsOH; (b) stained with OsO₄; (c) stained with CsOH and subsequently with OsO₄.

lution. The aggregate number of micelles increases during the evaporation process, but the micelle structures may be maintained intact until the solid structures are formed. Because each core-shell type polymer microsphere cannot interpenetrate with each other, due to repulsive effects between PAA·Et₃N and P4VP segments. The common PMS component chains in the shell portions are mutually compatible and form the continuous matrix [Fig. 9(b)]. Thus, the three-phase separated structure

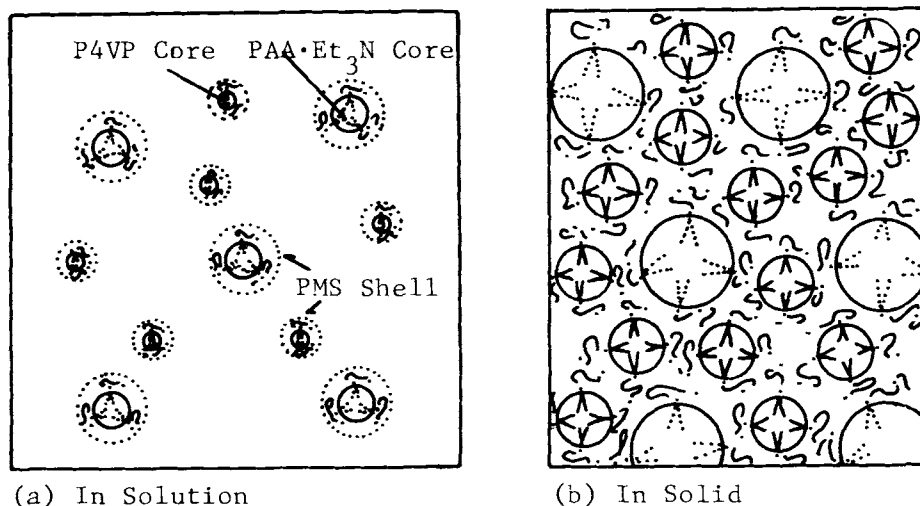


Figure 9 Schematic representations of molecular arrangements for GAS-E/GVS binary graft copolymer blend within the domains: (a) arrangement in solution; (b) arrangement in solid.

reveals BA/BC-type binary graft copolymer blends composed of the oppositely charged polyelectrolytes as trunks, when one side of free-acid or free-base components is converted into its salt. This three-phase separated structure in which positive- and negative-charged regions are dispersed in a PMS matrix is possible to use for thermal-reversible ion-exchange resins. The results obtained will be reported in the near future.

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