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Synthesis and Surface Formation of Three-Component Copolymers Having Polystyrene-*block*-poly(dimethylsiloxane) Graft Segments[†]

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ABSTRACT: Two types of three-component graft copolymers, in which the geometrical arrangement of the covalently-linked three polymer segments is inverse to the order of their surface energies, were synthesized, and their surface formation behavior was studied by means of contact angle and XPS measurements. Thus, poly(vinyl alcohol) (PVA)- and polyurethane (PU)-based three-component copolymers having polystyrene (PS)-*block*-poly(dimethylsiloxane) (PDMS) graft segments were synthesized by means of a macromonomer technique, in which PS-*block*-PDMS having a vinylsilane (**1**) or a diol (**2**) group at the end of the PDMS segment were prepared through the relevant end-capping reaction of a living PS-*block*-PDMS copolymer. The subsequent radical copolymerization of **1** with vinyl acetate, followed by the saponification of a poly(vinyl acetate), PVAc, segment produced a PVA-based copolymer having PS-*block*-PDMS graft segments (**4**). The polyaddition of **2** with diphenylmethyl diisocyanate, followed by the chain extension with butanediol produced a PU-based three-component copolymer (**5**). The topmost surfaces of the sample films of **4** and **5** were found to be covered with the PDMS component having the lowest surface energy, which is positioned between the PVA (or PU) and PS segments.

Introduction

Two-component block and graft copolymers, comprised of covalently connected immiscible polymer segments, generally result in microphase separation structure, and their surfaces tend to be covered with one component with the lower surface energy over the sublayer of another component with the higher surface energy. In addition, a polymer chain conformation at the surface may be distorted from that in bulk, since polymer molecules at the surface can interact not only with the surrounding identical molecules as in bulk but also with others in a different phase. Thus the block and graft copolymer film surfaces may realize unique properties due to the characteristic surface state of a polymer molecule. They can also provide a unique opportunity to elucidate the molecular-level mechanism of such important surface and interfacial phenomena as wetting,[1] rupturing (dewetting),[2,3] adhesion,[4] friction (lubrication),[5] etc. The dynamics of surface-induced phase separation in two-component block copolymers as well as in polymer blends is another subject of increasing interest.[6–10]

We have so far studied the surface formation and environmental response behavior of a series of two-component copolymers based on poly(vinyl alcohol), PVA, and on polyurethane, PU, as the main chain segments and polysiloxane,[11–13] polyether,[14,15] and polystyrene[16,17] as graft segments. They were prepared by means of a macromonomer technique, by which a graft copolymer having a well-defined graft segment length and graft density could be produced.[18] The subsequent surface studies on these graft copolymers demonstrated that the surface of graft copolymers is covered by the graft segment component having the lower surface energy on the sublayer of the higher surface energy component, i.e. PVA or PU. The thickness of the surface-covered layer of the graft component can be controlled by the total graft content in the copolymer. In addition, unique surface mobility even below the bulk glass transition temperature of the graft segment component in bulk was disclosed for the PS overlayer formed on the PVA sublayer by the examination of the temperature-dependent environmental response occurring with the change of the contacting medium from air to water of different temperatures.[16,19,20] The temperature-modulated environmental responses occurring on the surface of other block and graft copolymers of biomedical interest have been also reported.[21–23]

As an extension of the preceding studies, we report in the present paper on the synthesis and the surface formation of a *three-component* copolymer system, in which the geometrical order of the covalently-linked three segments is arranged inversely to the order of their surface energies. The three-component block and graft copolymer system is of increasing interest due to its unique and unusual morphology in bulk[24–26] and at the surface,[27] which is generated from the multiple combination of the repulsive and attractive interactions between the three segment components.[28–30] In addition, the combination of the two adversarial driving forces, such as wetting and phase separation, to induce the opposite thermodynamic states may lead to the formation of stable or metastable micro- and macroscopic structures of the unique morphology.[31,32]

In the present study, we have chosen three-component systems, i.e. poly(vinyl alcohol), PVA, or polyurethane, PU, as the main chain segment and polystyrene (PS)-*block*-poly(dimethylsiloxane) (PDMS) as a graft segment. The order of the surface energies of the three segments is PVA (or PU) > PS > PDMS. A PS-*block*-PDMS copolymer was prepared by a living polymerization technique,[33] and the surface of the copolymer was covered by the PDMS component.[34–36] Thus a polymerizable end group, i.e. a vinylsilane group for a chain

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[†] The paper is dedicated to Professor Kiyokazu Imai in honor of his 70th birthday.

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polymerization mechanism or a diol group for a step polymerization mechanism, was introduced at the end of the PDMS segment in the block copolymer. A block copolymer having a polymerizable group at the specific chain end of one segment component may be termed a "block macromonomer".[37-42] The subsequent radical copolymerization of the former with vinyl acetate, followed by the saponification of the poly(vinyl acetate) segment can produce a PVA-based three-component copolymer. The polyaddition reaction of the latter macromonomer with diisocyanate, followed by the chain extension with a low molecular weight diol compound can produce the corresponding PU-based three-component copolymer. Since the geometrical arrangement of the PVA (or PU), PS, and PDMS segments is inverse to the order of their surface energies, i.e. the PDMS segment is positioned between the PVA (or PU) and the PS segments, the surface structure formed under the influence of the two conflicting driving forces and the resulting surface properties will be of significant interest.

Experimental Section

1. Reagents. Styrene (Nacalai Tesque), dried over CaH_2 and distilled under reduced pressure, was passed through a column packed with aluminum oxide (Merck, aluminum oxide 90), stored over CaH_2 in a refrigerator, and distilled again immediately before use. Hexamethylcyclotrisiloxane, D_3 (Toshiba Silicone Co.), was distilled over CaH_2 just before use. *n*-Butyllithium (Nacalai Tesque, 1.6 mol/L in hexane) was filtered with a glass filter (G-4) and used after titration with 2,5-dimethoxybenzyl alcohol.[43] Chlorodimethylvinylsilane (Shin-Etsu Silicone Co.) was refluxed and distilled over CaH_2. 3-(3-(Chlorodimethylsilyl)propoxy)-1,2-bis(trimethylsiloxy)propane, CSBP, was synthesized and purified by the method reported before.[44] Vinyl acetate (Nacalai Tesque) was treated with 5% aqueous sodium hydrogen sulfite and distilled under reduced pressure in the presence of 2,2′-azobis(isobutyronitrile), AIBN, which was recrystallized from methanol. Potassium carbonate (Nacalai Tesque) was used as received. 4,4′-Diphenylmethyl diisocyanate, MDI, 1,4-butanediol, BD, and dimethylacetamide, DMAc (Nacalai Tesque), were refluxed over CaH_2 and distilled under reduced pressure. Tin(II) octylate, tin(II) 2-ethylhexanoate (Nacalai Tesque), was used as received. THF and benzene (Nacalai Tesque) were distilled from sodium/benzophenone just before use. Other reagents and solvents were purified by the conventional procedures.

2. Procedures. 2-1. Synthesis of PS-*block*-PDMS Macromonomers (1 and 2). Into a 100 mL round-bottom flask pre-evacuated and equipped with a three-way stopcock and a magnetic stirrer were introduced THF and benzene (30 mL in total, volume ratio is given in Table 1) by syringe under a dry N_2 atmosphere. Thereupon, 4.57 g (43.8 mmol) of freshly distilled styrene was added and the flask was placed in a bath thermostated at −50 °C. A prescribed amount of *n*-butyllithium solution was subsequently introduced by syringe under continuous stirring with a magnetic stirrer. The color of the solution turned immediately to orange, and the stirring was continued for 30 min. To this solution was added a 30 mL THF solution containing 4.58 g (20.6 mmol) of freshly distilled D_3, and the flask was placed in a bath thermostated at 25 °C. The reaction was continued for 3 h, while the orange color of the solution disappeared within 30 min. A 5-fold excess amount of chlorodimethylvinylsilane or CSBP was then added, and the solution was stirred for 1.5 h at 25 °C with the former, or for 2 h at 50 °C with the latter terminator. After solvents were removed by evacuation, the reaction product was isolated and purified by precipitation into methanol and finally freeze-dried from benzene solution.

2-2. Synthesis of PVA-Based Copolymer Having PS-*block*-PDMS Graft Segments. 2-2-1. Synthesis of PVAc-Based Copolymer Having PS-*block*-PDMS Graft Segments (3). Into an ampule pretreated with a sulfuric acid/dichromate solution were placed a weighed amount of **1**, 4.0 g (46.5 mmol) of vinyl acetate, 20 mg of AIBN, and 5.5 g of benzene, and the ampule was sealed after flushing with N_2 for 3 min. The ampule was then placed in a bath thermostated at 70 °C for 2.5 h, during which the ampule was swirled occasionally. The reaction mixture was then poured into 1 L of petroleum ether, and the recovered product was purified by reprecipitation either from a benzene/(petroleum ether + benzene; volume ratio 9/1) system when **1** from runs 1 and 2 in Table 1 were employed or from a benzene/petroleum ether system when **1** from run 3 in Table 1 was used. The reaction product was finally freeze-dried from benzene solution.

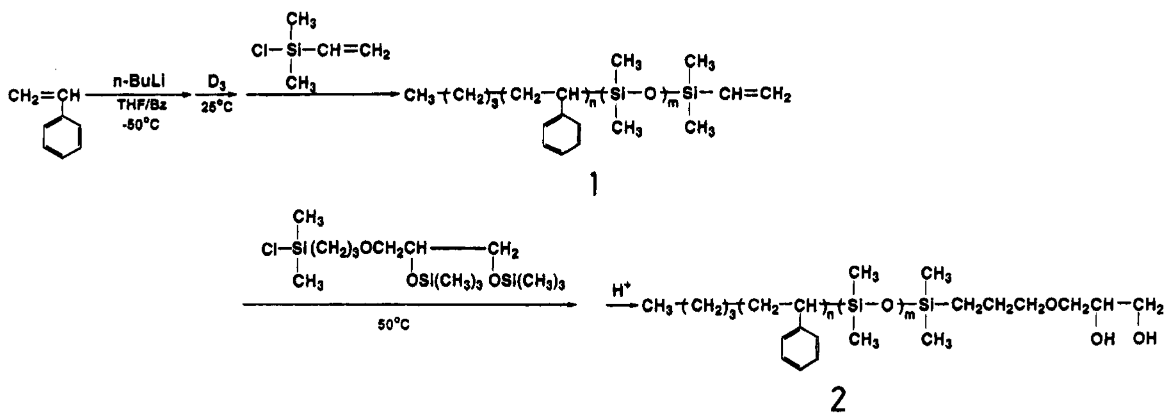
2-2-2. Synthesis of PVA-Based Copolymer Having PS-*block*-PDMS Graft Segments (4). In a 50 mL round-bottom flask equipped with a magnetic stirrer, a 22 mL methanol/THF mixture (volume ratio 10/1) solution containing 0.3 g of **3** was prepared. Thereupon, a 0.2 mL aqueous solution containing 25 mg of potassium carbonate was added and stirred at ambient temperature. A white precipitate was formed within a few minutes, while the stirring was continued for 110 min. The reaction product was isolated by filtration with a glass filter (G-4). The recovered product was then subjected to Soxhlet extraction with hot methanol for at least 10 h, and finally dried in vacuo at 60 °C for more than 24 h.

2-3. Synthesis of PU-Based Copolymer Having PS-*block*-PDMS Graft Segments (5). In a 50 mL round-bottom flask equipped with a three-way stopcock, a 15 mL DMAc solution containing a weighed amount of MDI was mixed with tin(II) octylate and triethylamine (both 1.0 wt % of the sum of MDI and **2**) under a N_2 atmosphere. Thereupon, a 10 mL DMAc solution containing a prescribed amount of **2** was introduced to react under stirring at 60 °C for 1 h, followed by the addition of a weighed amount of BD to continue the reaction for 7 h. The reaction product was recovered by pouring the mixture into 1 L of methanol and purified by reprecipitation from the DMAc/methanol system. The product was finally dried at 60 °C for more than 24 h.

3. Measurements. The 270 MHz ^{1}H-NMR spectra were recorded by means of a JEOL JNM GX-270 apparatus at 40 °C in $CDCl_3$ or at 100 °C in DMSO-d_6. Chemical shift values were calibrated from the residual proton signals of $CDCl_3$ (7.30 ppm) or DMSO-d_6 (2.50 ppm). IR spectra were taken on a Shimadzu FT-IR 8100 apparatus using a cast film sample on a NaCl plate from either a chloroform or DMSO solution. GPC measurements were performed using a Tosoh Model CCPD equipped with a RI8000 and UV8000 (254 nm) as detectors and a G3000HXL or a G4000HXL as a column using THF as eluent with a flow rate of 1.0 mL/min.

Contact angle measurements were carried out with a contact angle meter CA-A manufactured by Kyowa Kagaku Co. A water-in-air system was applied in the present study, where a water droplet was placed on the sample film surface in an environmental chamber.[16] The contact angle of each film sample was measured in at least six spots and four mean values were averaged. X-ray photoelectron spectroscopic (XPS) measurements were carried out with a Shimadzu ESCA 750 equipped with an ESCAPAC 760 data system.[16] Typical operation conditions were as follows; Mg $K\alpha_{1,2}$ radiation with 8 kV and 30 mA. The pressure in the instrumental chamber was kept below 3×10^{-5} Pa. Angle-dependent XPS measurements were carried out by using a sample holder adjusted to maintain the photoelectron escape angle at 45 and 15°. Normalized XPS peak intensities, which were used for comparing the elemental abundance at the surface of the film, were obtained by dividing the integral area by the relative strength factor based upon the calculated electron photoemission cross section of the various elements; those are $C_{1s} = 1.00$, $O_{1s} = 2.85$, $Si_{2p} = 0.87$, and $N_{1s} = 1.77$, respectively. Results were presented in terms of ratios of normalized XPS peak intensities, which should correspond to the elemental ratio at the surface region of the film. As a first-order approximation, escape depth variation with electron energy and spectrometer throughput as a function of energy were adjusted to cancel each other in the present Shimadzu XPS apparatus,[11] and therefore are not considered in the calculation of the relative abundance of elements. Samples of PVA-based copolymers as well as a PVA homopolymer for contact angle and XPS

Scheme 1



measurements were prepared by casting a DMSO solution (ca. 2.0 wt %) either on a clean glass plate (contact angle measurements) or on an aluminum sheet (XPS measurements), followed by evacuating at room temperature for 24 h, at 60 °C for 24 h, and finally at 120 °C for 48 h. Samples of PU-based copolymers as well as a PU homopolymer were prepared by a similar procedure from a DMAc solution. A PS-*block*-PDMS film sample was prepared from a THF solution (ca. 2.0 wt %) with evacuating at room temperature for 24 h and finally at 100 °C for 48 h.

Results and Discussion

1. Synthesis of PS-*block*-PDMS Macromonomers (1 and 2). Two types of polystyrene (PS)-*block*-poly(dimethylsiloxane) (PDMS) macromonomers having either a vinylsilane, **1**, or a diol end group, **2**, were prepared through the end-capping reaction of a living PS-*block*-PDMS, produced by a sequential copolymerization of styrene and D_3, having a lithium silanolate group at the chain end of the PDMS segment. The termination reaction of the living end group by a chlorosilane derivative can provide, as in the modification of the end group of a living PDMS itself,[45,46] various functional groups at the chain end of the PS-*block*-PDMS. Thus the reaction with either chlorodimethylvinylsilane or a chlorosilane derivative having a trimethylsilyl-protected diol group, i.e., 3-(3-(dimethylchlorosilyl)propoxy)-1,2-bis(trimethylsiloxy)propane, CSBP, was performed at an appropriate temperature (Scheme 1). The subsequent isolation and the deprotection of the trimethylsilyl group, if needed, produced uniform size PS-*block*-PDMS having a vinylsilane or a diol end group, **1** and **2**.

The 270 MHz ^{1}H-NMR spectra of **1** and **2** are shown in Figures 1 and 2, respectively. In both spectra, a signal from the methyl protons for the initiator (*n*-butyllithium) fragment is observed at 0.89 ppm as a triplet along with the overflowed main chain signals of the PS (around 1.0–2.5 and 6.5–7.5 ppm) and that of the PDMS segments (around 0 ppm). In addition, a signal of vinyl protons adjacent to silicon is observed for **1** at around 5.8–6.3 pm (Figure 1), and signals of methylene and methine protons adjacent to the ether and hydroxyl groups are observed for **2** around 3.4–3.9 ppm (Figure 2), respectively.

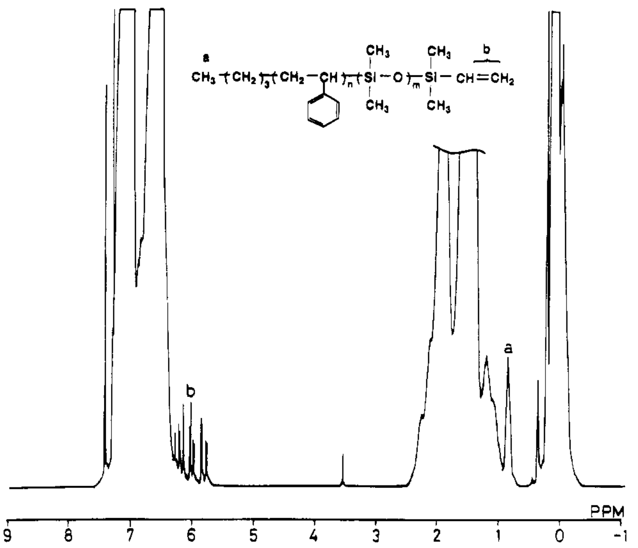


Figure 1. 270 MHz ^{1}H-NMR spectrum of **1**. Sample: run 2 in Table 1, $CDCl_3$, 40 °C.

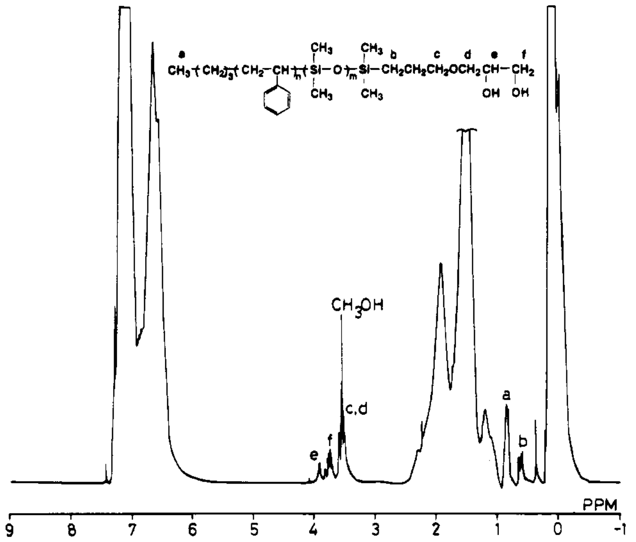


Figure 2. 270 MHz ^{1}H-NMR spectrum of **2**. Sample: run 5 in Table 1, $CDCl_3$, 40 °C.

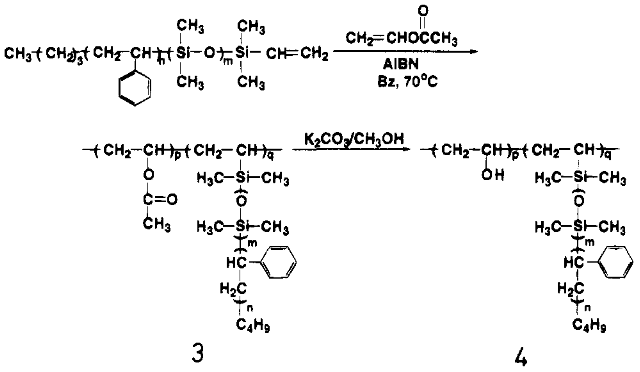
The results on the synthesis of **1** and **2** having various PS/PDMS segment compositions are listed in Table 1. By taking advantage of a sequential living polymerization technique, the total and the individual lengths of both the PS and the PDMS segments in the block copolymer could be controlled simply by adjusting the feed ratio of styrene and D_3 in the copolymerization. Thus two types of macromonomers having the total molecular weight of $(5-7) \times 10^3$ and having the PS/PDMS segment length ratios of ca. 1:0.5, 1:1, and 0.5:1 were prepared for further reaction. The end-capping efficiency was observed to be not always quantitative and could not be improved by several attempts under similar conditions. Since the end-capping reaction for the living PDMS homopolymer by identical chlorosilanes proceeded almost quantitatively, the presence of the PS

Table 1. Synthesis of Polystyrene-*block*-poly(dimethylsiloxane) Macromonomers (1 and 2)[a]

run	feed amount (mmol)			THF/benzene[b] (vol/vol)	terminating reagent[c]	yield (%)	MW ($\times10^3$)		polystyrene content[f]	end-capping efficiency[g] (%)	contact angle[h] (deg)
	styrene	D_3	C_4H_9Li				calc[d]	obs[e]			
1	48.1	11.3	1.25	2/1	V	88	5.5	5.7	0.65	100	106
2	43.8	20.6	1.14	2/1	V	90	7.3	9.1	0.45	100	107
3	34.2	32.0	1.78	1/1	V	83	5.2	7.3	0.31	71	105
4	38.5	9.0	1.00	2/1	D	88	5.4	6.3	0.67	27	104
5	43.3	20.4	1.13	2/1	D	62	6.5	5.4	0.53	100	101
6	20.0	18.8	1.04	1/1	D	64	4.9	7.0	0.32	54	111

[a] For the detailed reaction conditions, see Experimental Section. [b] 60 mL in total. [c] V: chlorodimethylvinylsilane. D: 3-(3-(chlorodimethylsilyl)propoxy)-1,2-bis(trimethylsiloxy)propane. [d] Calculated from the feed ratio between styrene and C_4H_9Li, and from the poly(dimethylsiloxane) content in **1** and **2**. [e] GPC with the calibration by polystyrene standards. [f] ^1H-NMR, $n/(n + m)$ in Scheme 1. [g] ^1H-NMR. [h] Water-in-air technique.

Scheme 2



segment appears to cause an adversarial effect in the end-capping reaction. An aggregation of PS-*block*-PDMS to result in a micelle formation under the present reaction conditions will be speculated.

2. Synthesis of PVA-Based Copolymer Having PS-*block*-PDMS Graft Segments (4). PS and PDMS macromonomers having a vinyl silane group copolymerize readily with vinyl acetate, a nonconjugated type monomer, to produce the corresponding poly(vinyl acetate) (PVAc)-*graft*-PS,[47] and PVAc-*graft*-PDMS,[45] respectively. In the present study, a radical copolymerization of **1** with vinyl acetate was carried out in benzene solution (Scheme 2). The reaction solution was homogeneous throughout the reaction in contrast to the phase separation observed in the copolymerization with the PDMS macromonomer.[45]

The 270 MHz ^1H-NMR spectrum of **3** showed, in addition to signals from the PS (around 6.5–7.1 and 1.8–2.0 ppm) and the PDMS (around 0 ppm) segments, those ascribed to the PVAc segment present at 4.9 and 2.0 ppm. IR spectral analysis of **3** also showed an absorption at 1750 cm^{-1} due to the ester group. Those are indicative of the formation of the three-component copolymer, **3**.

GPC traces of **3** together with the starting macromonomer, **1**, are compared in Figure 3. The uniformity, i.e. the narrow molecular weight distribution, of **1** and the higher molecular weight of the copolymerization product than that of **1** are demonstrated. It indicates also that the product is apparently free from the contamination of **1** after the purification by the reprecipitation technique.

The results on the synthesis of **3** having a series of PS-*block*-PDMS graft segments are listed in Table 2. The products having a molecular weight of more than 10^5 were obtained regardless of graft contents. The macromonomer, **1**, appears to be less reactive than vinyl acetate, since the PS and the PDMS contents in the product, **3**, are always lower than in the feed. The suppressed reactivity of **1** coincides with the observation in the copolymerization with the PDMS macromonomer,[45] while the enhanced reactivity was noted with the PS macromonomer.[47] The repulsive interaction between the PDMS and the PVAc segments prevails in the present copolymerization reaction with **1**. In the present copolymerization reaction, the conversion of vinyl acetate and **1** was deliberately controlled not to reach 30% in order to maintain the minimal compositional distribution in **3**.

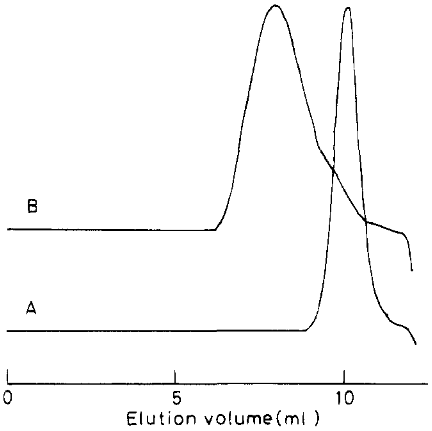


Figure 3. GPC traces of (A) **1** (sample: run 2 in Table 1) and (B) **3** (sample: run 5 in Table 2). Column: TSK G4000HXL. Eluent: THF, 1.0 mL/min.

The saponification reaction of the PVAc segment in a series of **3** was carried out in a methanol/THF mixture (Scheme 2). It was observed previously that the siloxane linkage in the PDMS segment in PVAc-*graft*-PDMS was extensively cleaved under the usual saponification conditions, i.e. with sodium hydroxide in methanol, while the saponification with potassium carbonate produced the corresponding PVA-*graft*-PDMS with minimal hydrolytic degradation of the PDMS segment.[45] Thus in the present study, the latter catalyst system with slightly modified conditions was applied in the saponification reaction.

The 270 MHz ^1H-NMR spectrum of a saponification product is shown in Figure 4. Signals due to the PVA segment such as a proton of a methine group at 3.92 ppm and that of a hydroxyl group as a tripet at 4.18, 4.42, and 4.59 ppm are observed together with those due to the PS and the PDMS segments. A small signal due to the residual PVAc segment is also detectable at around 5.0 ppm. The integration of the relevant signal areas can provide the degree of saponification as well as the relative content of the three segment components.

The results are summarized in Table 2. The degree of saponification reached near completion under the applied saponification conditions. On the other hand, the contents of the PS and the PDMS segments in the saponification products were comparably lower than

Table 2. Synthesis of Poly(vinyl acetate)- and Poly(vinyl alcohol)-Based Copolymers Having Polystyrene-*block*-poly(dimethylsiloxane) Graft Segments (3 and 4)[a]

		composition in feed (mol %)				composition in **3** (mol %)[d]				composition in **4** (mol %)[d]		
run	macromonomer type[b]	styrene unit	siloxane unit	yield of **3** (%)	MW (×10^5)[c]	styrene unit	siloxane unit	yield of **4**[e] (%)	saponification degree[d] (%)	styrene unit	siloxane unit	contact angle[f] (deg)
1	**1**-1	10.0	5.5	18	1.4	8.1	4.8	87	92	6.7	3.5	102
2	**1**-1	5.6	3.1	25	1.4	4.0	2.3	80	94	2.7	1.6	104
3	**1**-1	3.0	1.6	28	1.6	1.9	1.4	53	95	1.6	1.1	114
4	**1**-1	1.2	0.7	35	1.0	1.0	0.5	80	95	0.7	0.3	99
5	**1**-2	4.5	5.2	22	1.4	2.9	4.0	73	90	2.1	4.0	104
6	**1**-2	2.3	2.6	29	2.0	1.3	1.8	73	98	0.7	1.0	105
7	**1**-2	0.9	1.1	32	2.0	0.5	0.7	73	98	0.2	0.3	111
8	**1**-3	2.3	5.1	25	1.1	1.5	4.1	80	99	0.6	1.7	106
9	**1**-3	1.1	2.5	30	1.3	0.8	2.0	80	98	0.4	1.0	103
10	**1**-3	0.5	1.0	31	1.2	0.4	0.9	87	99	0.1	0.3	96

[a] For the detailed reaction conditions, see Experimental Section. [b] Macromonomer **1** from runs 1 (**1**-1), 2 (**1**-2), and 3 (**1**-3) in Table 1, respectively. [c] GPC with the calibration by polystyrene standards. [d] ^{1}H-NMR. [e] Calculated by assuming the complete saponification of poly(vinyl acetate) segment. [f] Water-in-air technique.

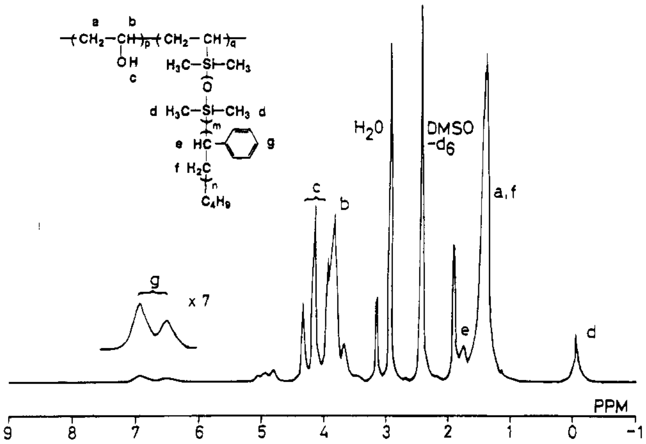


Figure 4. 270 MHz ^{1}H-NMR spectrum of **4**. Sample: run 5 in Table 2, DMSO-d_6, 100 °C.

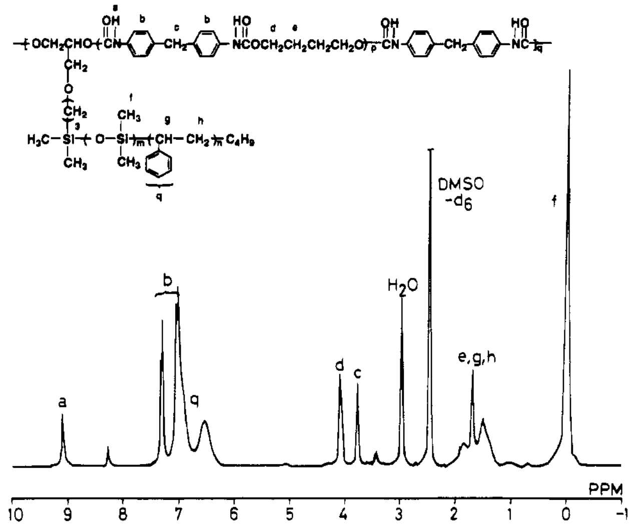
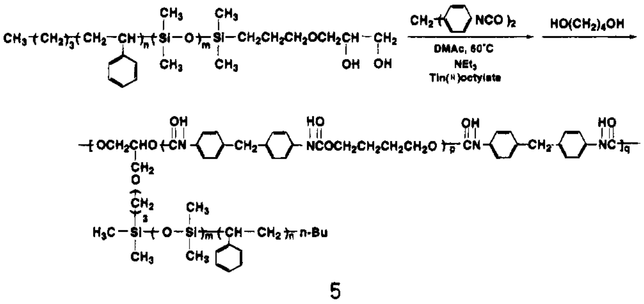


Figure 5. 270 MHz ^{1}H-NMR spectrum of **5**. Sample: run 4 in Table 3, DMSO-d_6, 100 °C.

those in the starting copolymer, **3**. The decrease in the PS segment content was more marginal than that in the PDMS segment content, indicating that the random cleavage of the PS-*block*-PDMS segment took place within the PDMS segment. IR spectroscopic analysis of the saponification product showed an absorption at 3370 cm^{-1} due to the hydroxyl groups in **4** along with the decreased absorption at 1740 cm^{-1} due to the residual ester groups in **4**.

3. Synthesis of PU-Based Copolymer Having PS-*block*-PDMS Graft Segments (5). PS and PDMS macromonomers having a diol end group were utilized to produce the relevant PU-based two-component graft copolymers.[44,48] In the present study, the PS-*block*-PDMS macromonomer having a diol end group, **2**, was subjected to a polyaddition reaction with diphenylmethyl diisocyanate, MDI, followed by chain extension with butanediol, BD, in various MDI/BD ratios to produce a series of PU-based three-component copolymers, **5** (Scheme 3).

Scheme 3



5

The 270 MHz ^{1}H-NMR spectrum of the polyaddition product is shown in Figure 5. In addition to signals due to the PDMS segment at around 0 ppm, those assignable to the polyurethane segment are visible, i.e. a urethane proton at 9.10 ppm, phenyl ring protons at around 7.3 ppm which are apparently overlapped with signals due to the PS segment from **2**, and diphenylmethylene protons at 3.80 ppm, respectively. The IR inspection of the polyaddition product and the relevant PS-*block*-PDMS macromonomer, **2**, also indicated the formation of polyurethane product, **5**, by an absorption at 1700 cm^{-1} due to urethane carbonyl groups. GPC examination of the product also showed the formation of the polyaddition product, **5**, having a molecular weight higher than that of the original macromonomer, **2** with the concurrent formation of a minor portion of polyurethane oligomer having the lower molecular weight.

The results on the synthesis of **5** are collected in Table 3. The contents of the PS and the PDMS segments in the isolated products were nearly identical to those in the feed for the samples of high recovery yields. The low recovery yield in a few runs is thought to be due to the evolution of compositional distribution during the polyaddition reaction: A part of the product, **5**, was thus

Table 3. Synthesis of Polyurethane-Based Copolymers Having Polystyrene-*block*-poly(dimethylsiloxane) Graft Segments (5)[a]

run	macromonomer type[b]	molar ratio in feed 2/MDI/BD	composition in feed (wt %) styrene unit	composition in feed (wt %) siloxane unit	yield (%)	composition in 5 (wt %)[c] styrene unit	composition in 5 (wt %)[c] siloxane unit	contact angle (deg)[d]
1	**2-4**	1/50/49	20.0	7.0	36	14.0	4.6	101
2	**2-4**	1/100/99	12.0	4.0	62	9.2	2.7	102
3	**2-4**	1/200/199	6.3	2.2	48	4.7	1.2	103
4	**2-5**	1/10/9	38.0	24.0	74	42.0	25.0	*e*
5	**2-5**	1/50/49	15.0	9.2	67	17.0	8.4	112
6	**2-5**	1/100/99	8.5	5.2	86	8.6	4.4	103
7	**2-5**	1/200/199	4.6	2.8	87	4.7	2.1	103
8	**2-6**	1/50/49	12.0	18.0	70	13.0	22.0	104
9	**2-6**	1/100/99	6.8	10.0	79	8.3	13.0	104
10	**2-6**	1/200/199	3.7	5.5	47	3.3	7.4	102

[a] For the detailed reaction conditions, see Experimental Section. [b] Macromonomer **2** from run 4 (**2-4**), 5 (**2-5**), and 6 (**2-6**) in Table 1, respectively. [c] ^{1}H-NMR [d] Water-in-air technique. [e] Not determined.

lost during the isolation procedure by the reprecipitation technique. Both primary and secondary hydroxyl groups in **2** appear to react with MDI during the first stage of the polyaddition reaction to produce the PU-based three-component copolymer, **5**.

4. Surface Formation of PVA- and PU-Based Copolymers Having PS-*block*-PDMS Graft Segments. Contact angle and XPS inspections on the dry surface of cast film samples of a series of PVA- and PU-based copolymers having PS-*block*-PDMS graft segments, **4** and **5**, were performed with reference to those of the PS-*block*-PDMS copolymer. Copolymer samples were rigorously purified by the repeated precipitation procedure before the film preparation.

Film sample surfaces of **4** and **5** were studied first by means of a contact angle measurement with a water-in-air technique. The results of the contact angle measurements for a series of **4** and **5** having various graft segment contents and graft segment compositions, as well as on those for a series of macromonomers, **1** and **2**, are listed in the last column in Tables 1–3, respectively. The contact angle measurement with a water droplet can conveniently distinguish the surfaces of PVA homopolymer (50°) from that of either PS (87°) PDMS homopolymers (107°), and of the PU homopolymer (85°) from that of the PDMS homopolymer in the dry state. The contact angles for a series of the sample films of **4** and **5** as well as the macromonomers, **1** and **2**, were found to be substantially higher than those of PVA, PU, and PS and nearly identical to that of the PDMS homopolymer, except for **4** and **5** with very low graft segment contents.

Since the contact angle measurement can sense the top few angstroms of the organic surfaces, the topmost surface of the sample films of **4** and **5** is believed to be covered with the PDMS component, which is positioned between the PVA (or PU) and the PS segments. The substantially lower surface tension of PDMS (20 dyn/cm)[49] than those of other components, i.e. 33–36 dyn/cm for PS,[49] 37 dyn/cm for PVA,[49] and 39 dyn/cm for PU,[49] respectively, can promote the relocation of the PDMS segment toward the topmost surface despite its unfavorable geometrical confinement.

XPS analysis on cast film samples of a series of **4** and **5** was then carried out to compare with that of the starting macromonomer, **1** and **2**. Full-range XPS inspection of these sample films showed peaks due solely to C_{1s}, O_{1s}, Si_{2s}, and Si_{2p} for **4** and an additional N_{1s} peak for **5**, indicating that the sample surface was free from contamination by catalyst residue (Sn used for the preparation of **5**) or by other incidental sources.

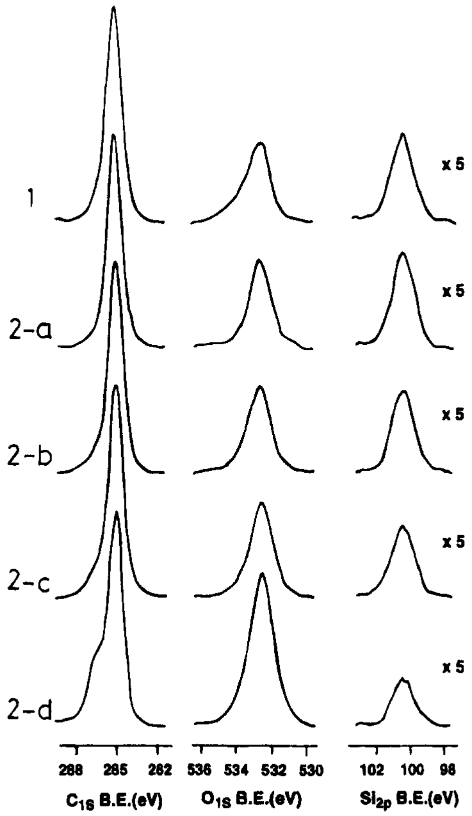


Figure 6. C_{1s}, O_{1s}, and Si_{2p} XPS results for (1) **1** (sample: run 1 in Table 1) and (2a–d) **4** having different graft contents (samples: (a) run 1, (b) run 2, (c) run 3, and (d) run 4 in Table 2).

XPS results for the C_{1s}, O_{1s}, and Si_{2p} regions of **4** having different graft contents are shown in Figure 6, together with that of the relevant macromonomer, **1**. The ratio of the intensity of C_{1s}, O_{1s}, and Si_{2p} signals for the surface of **4** (apparent elemental ratios of O_{1s}/C_{1s} = 0.17 and Si_{2p}/C_{1s} = 0.13 for 2a in Figure 6) was observed to be nearly identical to that for **1** (O_{1s}/C_{1s} = 0.17 and Si_{2p}/C_{1s} = 0.11), except for the samples of very low graft segment content (2d in Figure 6). Thus it can be concluded that the sample surfaces, within the depth detectable by the XPS, i.e. 50–100 Å, of a series of **4** having more than a few mole percent of the graft segment contents are dominated with the PS-*block*-PDMS component. Topmost surfaces of PDMS-containing block and graft copolymers, including PS-*block*-PDMS, are commonly covered by the PDMS component,[34,35] and a topmost surface of the PVA-*graft*-

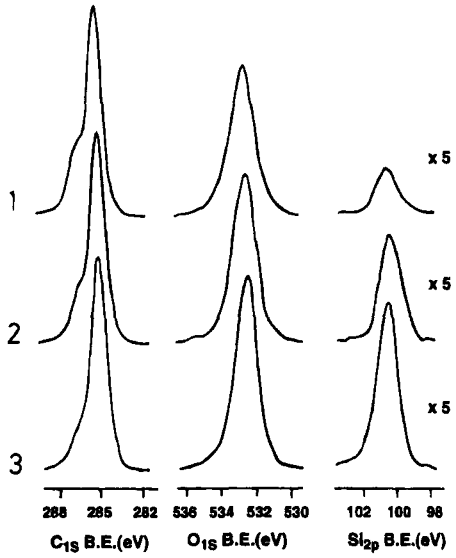


Figure 7. C_{1s}, O_{1s}, and Si_{2p} XPS results for **4** having different graft segment compositions. Samples: (1) run 4, (2) run 6, and (3) run 8 in Table 2.

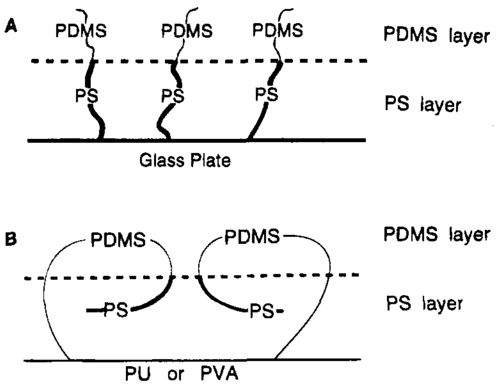


Figure 8. Schematic pictures of the surface of (A) PS-*block*-PDMS and (B) PVA (or PU)-based copolymers having PS-*block*-PDMS graft segments.

PS is covered by the PS component.[16] The surface tensions of both PS and PDMS segments are notably lower than that of the PVA segment to promote the surface accumulation of the PS-*block*-PDMS component on the PVA sublayer.

XPS results on a series of **4** having the PS-*block*-PDMS of different segment compositions are shown in Figure 7. The relative intensity of the Si_{2p} signal was observed to be higher for the samples having the higher PDMS contents (Si_{2p}/C_{1s} = 0.06 for 1, 0.13 for 2, and 0.19 for 3 in Figure 7). This indicates that the surface of a series of **4** is dominated with the PS-*block*-PDMS component. For the samples of the low graft segment contents, a shoulder peak for the C_{1s} signal, assignable to the C−O linkage, and the enhanced intensity of the O_{1s} signal were observed to indicate that a small portion of the PVA component was also present at the surface.

By combining both contact angle and XPS results on a series of **4**, it can be concluded that the surface of 50–100 Å depth on the sample films of **4** is dominated by the PS-*block*-PDMS component formed on the PVA sublayer, while the topmost surface of a few angstroms depth is covered by the PDMS component. Since the PDMS segment in **4** is positioned between the PS and the PDMS segments, such a surface morphology as shown in Figure 8 is likely be the case in the present three-component system due to the conflict of a thermodynamic driving force with a geometric restriction.

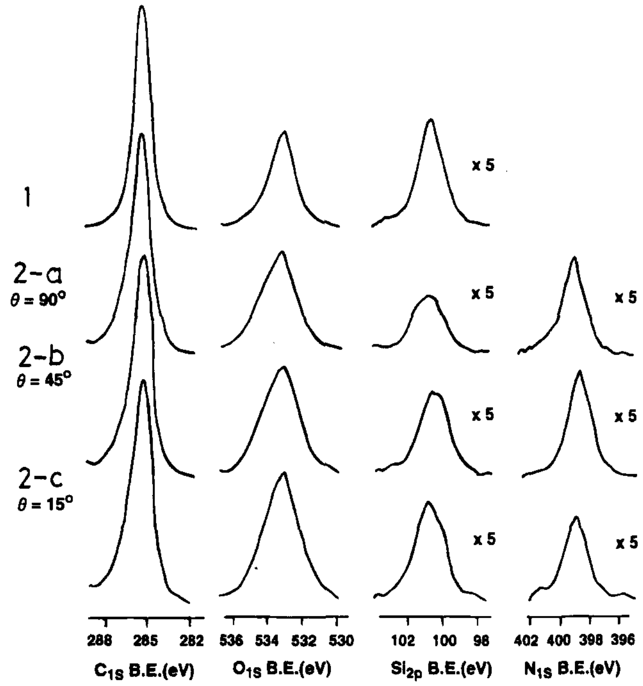


Figure 9. C_{1s}, O_{1s}, Si_{2p}, and N_{1s} XPS results for (1) **2** (sample: run 4 in Table 1) and (2a–c) **5** (sample: run 1 in Table 3). The escape angle of the photoelectron is given in degrees.

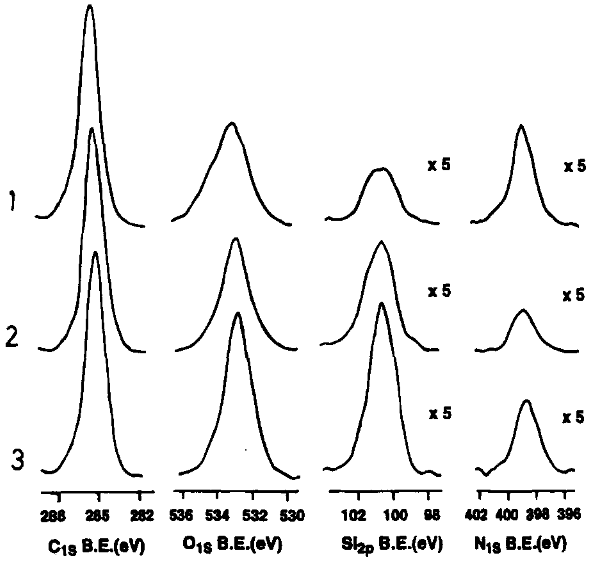


Figure 10. C_{1s}, O_{1s}, Si_{2p}, and N_{1s} XPS results for **5** having different graft segment compositions. Samples: (1) run 1, (2) run 5, and (3) run 8 in Table 3.

XPS results for the C_{1s}, O_{1s}, Si_{2p}, and N_{1s} regions of **5** are summarized in Figures 9 and 10. The results of angle-dependent XPS measurements are collected in Figure 9, in which the escape angle of photoelectrons was changed from 90 to 15° in order to monitor the elemental ratio closer to the sample surface of **5**. Although the ratio of the intensity of C_{1s}, O_{1s}, and Si_{2p} for **5** (O_{1s}/C_{1s} = 0.25 and Si_{2p}/C_{1s} = 0.11 for 2c in Figure 9) was close to that for the PS-*block*-PDMS macromonomer, **2** (O_{1s}/C_{1s} = 0.19 and Si_{2p}/C_{1s} = 0.13), an additional N_{1s} signal with a measurable intensity (N_{1s}/C_{1s} = 0.044 for 2c in Figure 9) was observed even at the topmost surface with the escape angle of 15° (10–20 Å). The PU component is thus present even in the vicinity of the topmost surface. The intensity of the Si_{2p} signal increased closer to the topmost surface, implying the topmost surface of **5** is covered by the PDMS component in accord with the contact angle results (Table 3). The difference in the surface tensions between the PU and the PS segments is minimal and a partial phase mixing was suggested in the previous PU-*graft*-PS two-component system.[44] This is in contrast to the relevant PVA-based three-component system, in which the three components are highly immiscible with each other. The different combinations of the interactions between segments in the three-component copolymers, **4** and **5**, apparently influenced the microscopic morphology formed on their surfaces.

XPS results on a series of **5** having the PS-*block*-PDMS segment of different compositions are shown in Figure 10. As observed in the relevant PVA-based copolymer system (Figure 7), the relative intensity of the Si_{2p} signal increased with the increase of the PDMS content ($Si_{2p}/C_{1s} = 0.07$ for 1, 0.14 for 2, and 0.18 for 3 in Figure 10), showing the surface accumulation of the PS-*block*-PDMS component on the PU sublayer.

The combined results of contact angle and XPS measurements for **5** indicate that a major composition of the surface of 50−100 Å depth is the PS-*block*-PDMS component, while the PU component is also present as a minor composition presumably through the phase mixing with the PS component. On the other hand, the topmost surface of a few angstroms depth is covered by the PDMS component. Thus, the surface morphology shown in Figure 10 for the PVA-based three-component copolymer system appears to be applied also for the PU-based copolymer system.

In conclusion, the present study revealed unique surface features realized by the precisely designed three-component copolymer systems and provides new insight for the molecular design of polymeric material surfaces applied from bioengineering to tribology.

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