Surface Characteristics of Fluoroalkylsilicone—Poly(methyl Methacrylate) Block Copolymers and Their PMMA Blends

HIROSHI INOUE, AKIHIRO MATSUMOTO, KIMIHIRO MATSUKAWA, AKIRA UEDA, and SUSUMU NAGAI, *Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536, Japan*

Synopsis

Surface properties of fluoroalkylsilicone—poly(methyl methacrylate) block copolymers and their poly(methyl methacrylate) (PMMA) blends have been intensively studied to draw a relationship between surface segregation behavior and adhesion performance. The fluoroalkylsilicone—PMMA block copolymers containing three kinds of fluoroalkyl side chains (i.e., 3,3,3-trifluoropropyl) ($CF_3CH_2CH_2$-, abbreviated as TFP), tridecafluoro-1,1,2,2-tetrahydrooctyl[$F_3C(CF_2)_5CH_2CH_2$-, TFO], and heptadecafluoro-1,1,2,2-tetrahydrodecyl groups [$F_3C(CF_2)_7CH_2CH_2$-, HFD] on the siloxane chains were prepared according to the macroazoinitiator method. Contact angle measurement and X-ray photoelectron spectroscopy (or ESCA) were used to obtain structural information on the surface of the solution-cast films. A significant effect of fluoroalkyl groups on the surface accumulation not only in silicon but also fluorine atoms were observed for relatively long fluoroalkyl side chains (i.e., TFO and HFD). On the contrary, TFP group was found to be effective to orient to the hydrophilic surfaces (i.e., glass-side surfaces). The surface accumulation of fluoroalkyl groups in the films was also reflected by the 180° peel strength against pressure-sensitive adhesives as a measure of the adhesion performance. These results indicated that incorporation of relatively long fluoroalkyl groups much enhanced the surface hydrophobicity (and/or oleophobicity) of solution-cast films in addition to that of the siloxane-enriched surfaces. The composition and orientation of the functional groups on the surface were also speculated based on ESCA data.

INTRODUCTION

Surface segregation behavior of block copolymers are of very much interest in fields of adhesion, coating, printing, friction, biocompatibility and so on.

It was reported in previous papers[1,2] that the polysiloxane segments of polydimethylsiloxane—poly(methyl methacrylate) block copolymers (PDMS-b-PMMA) derived from poly(azo-containing siloxaneamides) (abbreviated as PASAs) and their PMMA blends (PDMS-b-PMMA/PMMA) were accumulated on air-side surfaces of the solution-cast films as revealed by water contact angle measurements and ESCA (electron spectroscopy for chemical analysis) or X-ray photoelectron spectroscopy. It was concluded that the most flexible polydimethylsiloxane segments were readily phase-separated and moved to the top most surface because of their low surface energy. In those works, a significant effect of siloxane chain length (SCL) on the surface accumulation behavior of the siloxane segments was also emphasized. The preferential surface accumulation of the siloxane segments resulted in a steep decrease in peel strength
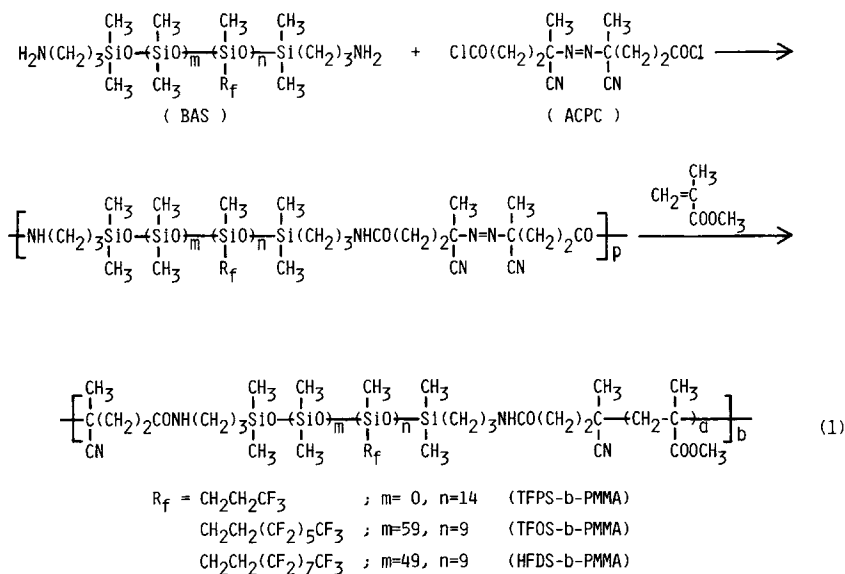
against pressure-sensitive adhesive tapes.[2] More interestingly, the peel strength was unequivocally correlated with the siloxane surface concentration estimated from ESCA data.

Similar surface segregation of siloxane segments for some types of siloxane-containing block copolymers was reported by McGrath and others.[3–8] It was also noticed that the siloxane surface segregation substantially depended on the block length of siloxane chain (i.e., siloxane chain length (SCL)), and the rate to attain an equilibrium surface. The latter was an important factor for surface segregation, as revealed from the difference of the specimen preparation methods (e.g., solvent-casting and heat press[2,3,4,6]).

Incorporation of low-surface-energy fluoroalkyl groups into siloxane segments may be anticipated to enhance surface accumulation of their segments to impart not only hydrophobic but also oleophobic surfaces.

In this work, several fluoroalkylsilicone—PMMA block copolymers were prepared via polysiloxane(azobiscyanopentanamide)s, as shown in eq. (1).

The effect of fluoroalkylsiloxane chains on the surface properties of their silicone—PMMA block copolymers/PMMA blend films were intensively studied by means of contact angle, ESCA and peel strength measurements. Three kinds of fluoro-alkyl groups [$CF_3CH_2CH_2$- (abbreviated as TFP), $CF_3(CF_2)_5CH_2CH_2$- (TFO), and $CF_3(CF_2)_7CH_2CH_2$- (HFD)] were chosen as siloxane side chains to evaluate an effect of side chain length. Our attention was, furthermore, focused on the dependence of surface accumulation of siloxane and fluoroalkyl groups on the adhesion performance.

$$R_f = CH_2CH_2CF_3 \quad ; \; m=0, \; n=14 \quad (TFPS\text{-}b\text{-}PMMA)$$
$$CH_2CH_2(CF_2)_5CF_3 \quad ; \; m=59, \; n=9 \quad (TFOS\text{-}b\text{-}PMMA)$$
$$CH_2CH_2(CF_2)_7CF_3 \quad ; \; m=49, \; n=9 \quad (HFDS\text{-}b\text{-}PMMA)$$

EXPERIMENTAL

Materials

Preparation of PDMS-b-PMMA having a SCL of 9800 was described elsewhere,[9] [PDMS(9800)-b-PMMA], Mn = 107000, Mw = 676000, Mw/Mn

= 6.31, 100 $SiMe_2O/(MMA + SiMe_2O)$ = 23.3 mol % (18.4 wt %). 3,3,3-Trifluoropropyl-silicone—PMMA block copolymers (TFPS-b-PMMA) were synthesized according to the similar method.[9]

A commercial extrusion grade poly(methyl methacrylate) (PMMA) for blend was successively purified by reprecipitation from a chloroform—methanol system, and Soxhlet extraction with petroleum ether. Mn = 63000, Mw = 134000, Mw/Mn = 2.13 (GPC).

Preparation of α,ω-Bis(3-aminopropyldimethylsilyl)-poly(fluoroalkyl-1-methylsiloxane-co-dimethylsiloxane)s

As an example, the preparation of α,ω-bis(3-aminopropyl-dimethylsilyl)poly(tridecafluoro-1,1,2,2-tetrahydrooctyl-1-methyl siloxane-co-dimethylsiloxane) (BAS-TFO) is shown as follows:

A solution of 10 g (22 mmol) of tridecafluoro-1,1,2,2-tetrahydrooctyl-1-methyl dichlorosilane (Petrarch Systems, Chisso Co.) and 20 mL of diethylether was hydrolyzed by pouring into a large amount of diethylether/ice water mixture. The diethylether solution was washed with water and dried on anhydrous sodium sulfate. After evaporation of the solution, the siloxane oligomer (tridecafluoro-1,1,2,2-tetrahydrooctyl-1-methylsiloxane, TFO-MS) was obtained as a residue.

8.02 g (20 mmol based on SiO unit) of TFO-MS was mixed with 1.02 g (4.2 mmol) of bis(3-aminopropyldimethyl)disiloxane (Chisso Co.) in a 100 mL two-necked flask with a serum cap and a reflux condenser having a CaCl₂ tube, respectively. About 10 drops of the polymerization catalyst derived from trimethylbenzylammonium hydroxide and octamethylcyclotetrasiloxane[10] was injected into the solution. Then, the solution was heated at 75°C for 43 h with stirring under dry nitrogen atmosphere. After further heating at 130°C for 3 h, 50 mL of methanol was added to the solution and the mixture was shaken in a separatory funnel. Then, the bottom layer was washed with water and dried over anhydrous sodium sulfate. The volatile liquid was distilled off at 160°C under reduced pressure. α,ω-Bis(3-aminopropyldimethylsilyl)poly(tridecafluoro-1,1,2,2-tetrahydrooctyl-1-methylsiloxane) (BAS-TFOS) was obtained as a residue in 6.48 g yield (72%). The polysiloxane (BAS-TFOS) was little soluble in conventional solvents, such as, toluene, benzene, tetrahydrofuran, chloroform and ethyl acetate; therefore, it was impossible to determine its molecular weight.

A soluble polysiloxane was obtained by the equilibrium copolymerization with octamethylcyclotetrasiloxane in a following manner. In a two-necked 100 mL flask, a mixture of 6.00 g of BAS-TFOS and 6.43 g (22 mmol) of octamethylcyclotetrasiloxane was heated in the presence of 0.1 g of benzyltrimethylammonium hydroxide at 80°C for 20 h in a stream of dry nitrogen, and then at 150°C for 1 h. The resulting solution was washed with methanol in a separatory funnel, and then shaken with addition of diethylether and water. The diethyl ether layer was dried over anhydrous sodium sulfate. Evaporation of diethylether resulted in 10.17 g of pale yellow liquid, α,ω-bis(3-aminopropyldimethylsilyl) poly (tridecafluoro-1,1,2,2-tetrahydrooctyl-1-methylsiloxane-co-dimethylsiloxane) (BAS-TFO). BAS-TFO was soluble in chloroform, tetrahydrofuran and toluene. The molecular weight was determined by gel permeation chro-

matography (GPC) to be Mn = 8200, Mw = 17000, and Mw/Mn = 2.12. The GPC curve also revealed the contamination of a small amount of three- and four-membered cyclic fluoroalkylsiloxanes (TFO-MS), causing difficulty to purify BAS-TFO. However, the contaminants were removed on the basis of solubility difference after the following polycondensation.

α,ω-Bis(3-aminopropyldimethylsilyl)poly(heptadecafluoro-1,1,2,2-tetrahydrodecyl-1-methylsiloxane-co-dimethylsiloxane) (BAS-HFD) was prepared by the method similar to that of BAS-TFO, Mn = 8400, Mw = 15000, and Mw/Mn = 1.78 (GPC).

Polycondensation of α,ω-Bis(3-aminopropyldimethylsilyl)poly(fluoroalkyl-1-methylsiloxane-co-dimethylsiloxane) with Azobiscyanopentanoyl chloride (ACPC)

An example of the preparation of TFO group-containing poly(azobiscyanopentanamide) (PASA-TFO) is described as follows:

In a dried 200 mL four-necked and round-bottomed flask fitted with a motor-driven stirrer, a thermometer, a dropping funnel, and a reflux condenser having a CaCl$_2$ tube, 8.20 g (1.0 mmol) of BAS-TFO, 0.20 g (2.0 mmol) of triethylamine and 10 mL of chloroform were placed. After the flask was cooled in an ice-water bath at 0–5°C, 0.32 g (1.0 mmol) of azobiscyanopentanoyl chloride in 10 mL of chloroform was added dropwise through the dropping funnel over 30 min with stirring. The solution viscosity gradually increased as the polycondensation proceeded. Stirring was further continued at room temperature (ca. 20°C) for 1 h and then at 30°C for 1 h.

The resulting viscous solution was diluted with 150 mL of chloroform and transferred to a separatory funnel. Then, the solution was mixed with ca. 50 mL of water to dissolve the salt and other water-soluble impurities, and the two layers were separated. The washing was repeated twice to insure the removal of impurities from the product. The chloroform layer was dried with anhydrous sodium sulfate by allowing it to stand in a refrigerator over night. After evaporation of volatile materials and then washing with acetone, the pale yellow and very viscous liquid, PASA-TFO, was obtained in 7.71 g (91%) yield. PASA-TFO was stored in a refrigerator to avoid thermal decomposition. Mn = 44000, Mw = 70000, and Mw/Mn = 1.59 (GPC).

HFD-group-containing poly(azobiscyanopentanamide) (PASA-HFD) was also synthesized according to the method similar to that of PASA-TFO, keeping equimolar conditions for BAS-HFD and ACPC. Mn = 44000, Mw = 220000 and Mw/Mn = 5.03.

Polymerization of Methyl Methacrylate with PASAs

Preparation of TFO group-containing silicone—PMMA block copolymer (TFOS-b-PMMA) was done with the following procedure, as an example:

In a 200 mL three-necked and round-bottomed flask equipped with a reflux condenser having a CaCl$_2$ tube, a motor-driven stirrer and a N$_2$ gas inlet, 4.00 g (0.49 mmol azo group) of PASA-TFO was dissolved in 20.00 g (200 mmol) of methyl methacrylate and 20 mL of methylethylketone. Into the resulting homogeneous solution, dry nitrogen gas was introduced and the solution was heated at 80°C. As the polymerization proceeded, the solution viscosity gradually

increased. After 5 h reaction time, the viscous polymer solution was diluted with chloroform and was poured in a large amount of methanol to precipitate the polymer. The polymer thus prepared was dried in vacuum at 45°C for 10 h to yield 17.85 g (74%). The polymer was purified by petroleum ether extraction for 24 h, followed by reprecipitation using chloroform-methanol system. Mn = 37000, Mw = 130000, Mw/Mn = 3.34 (GPC), and 100 (SiO)/[(SiO) + MMA] = 18.7 wt % (from ^{1}H-NMR).

The similar procedure was also applied to the synthesis of HFD group-containing silicone—PMMA block copolymer (HFDS-b-PMMA). Mn = 49000, Mw = 800000, Mw/Mn = 16.5 (GPC), and 100(SiO)/[(SiO) + (MMA)] = 18.5 wt %.

Preparation of Cast Films

Mixtures of the block copolymers and PMMA in various compositions were dissolved in chloroform at 5% concentration. The solution were cast on clean glass culture dishes, and allowed to stand for almost two days. The blend films were further dried at 40°C and reduced pressure for more than one day after detached from the glass dishes. The thickness of the blend films was ca. 0.3 mm for PDMS(9800)-b-PMMA/PMMA, TFOS-b-PMMA/PMMA and HFDS-b-PMMA/PMMA systems, and ca. 0.45 mm for TFPS-b-PMMA/PMMA systems.

Analysis and Testing

^{1}H-NMR spectra were measured with a JEOL FT-NMR spectrometer FX-90 (90 MHz) using DCCl$_3$ solution at 50°C to determine the siloxane contents, 100(SiO)/[(SiO) + (MMA)] in mol % or wt %.

Molecular weights (Mn and Mw) and their distributions were determined by gel permeation chromatography (GPC) by the use of a Waters liquid chromatograph 150-C (refractive index detector; Shodex columns 80M, 80M, and 802.5 in this series; tetrahydrofuran of 1 mL/min. at 40°C and 32 bars). The molecular weights were calibrated with nine polystyrene standards (Pressure Chemical Co.).

Contact angles of the blend films were measured by a sessile drop method using an Erma contact anglemeter Model II at 23°C, and 50% RH. All measurements on both the air-side and glass-side surfaces were conducted within one minute after placing drops of liquids on the film surfaces. Critical surface tensions of the films were evaluated on the basis of surface tension data of some hydric liquids,[11] γ_L(dyne/cm), water 72.8, glycerol 63.4, formamide 58.2, thioglycol 54.0 polyethylene glycol-200 43.5, dipropylene glycol 33.9.

Electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy of the film surfaces was measured with a Shimadzu X-ray photoelectron spectrometer ESCA 750 accompanied by a data processor ESCAPAC 760. A Mg anode was used as X-ray source under vacuum at 2×10^{-7} Torr (6kV-30mA). A take-off angle for film samples was 90°. The ESCA peak intensity was corrected by dividing the integrated numbers of photoelectron counts by the relative strength factor (i.e., photoelectron cross-section).

A testing method for 180° peel strength as a measure of adhesion performance was similar to JIS Z 0237. The films were adhered with a Scotch pressure-

sensitive adhesive tape #250 (Sumitomo 3M Co.) with a width of 19 mm under load of 5 kg roller. The 180° peel testing was done with a Shimadzu Autograph S-500-D of a 100 mm/min crosshead speed. The peel data were averaged for two specimens.

RESULTS AND DISCUSSION

Synthesis of Fluoroalkylsilicone—PMMA Block Copolymers

The fluoroalkylsilicone—PMMA block copolymers were prepared by radical polymerization of methyl methacrylate (MMA) using the poly(azo-containing)siloxaneamides (PASAs) obtained from polycondensation of α,ω-bis(3-aminopropyldimethylsilyl)-poly(fluoroalkylmethylsiloxane)s(BAS) with azo-biscyanopentanoyl chloride (ACPC), similar to the procedures reported elsewhere.[9] In this work, three kind of fluoroalkyl groups (i.e., 3,3,3-trifluoropropyl (TFP), tridecafluoro-1,1,2,2-tetrahydrooctyl (TFO) and heptadecafluoro-1,1,2,2-tetrahydrodecyl (HFD)) were used to study the effect of the side chain length on their surface properties. In the case of TFO- and HFD-group-containing silicone—PMMA block copolymers, the copolysiloxanes were used as the silicone segments to improve solubility, and to attain homogeneous polymerization and well-defined characterization of block copolymers.

Synthetic results of several PASAs having fluoroalkyl side chains are summarized in Table I. These fluoroalkyl-containing PASAs were soluble in appropriate solutions consisted of MMA and a solvent. The polymerization of MMA was carried out with these PASAs to form the fluoroalkylsilicone—PMMA block copolymers. The polymerization results are shown in Table II.

GPC curves of BAS-TFO, PASA-TFO and block copolymer (TFOS-b-PMMA) are illustrated in Figure 1, as examples.

Although the presence of lower molecular weight contaminants, three- and four-membered cyclic siloxanes (TFO-MS or HFD-MS) in BAS-TFO or BAS-HFD was detected, they were reacted with ACPC in apparent equimolar conditions without further purification. The low molecular weight impurities were removed after acetone washing of the relatively high molecular weight PASAs, suggesting little effect of cyclic siloxanes on polycondensation. ^{1}H-NMR and IR spectra, and GPC were employed for characterization of these products.

The fluoroalkylsilicone—PMMA block copolymers thus prepared (TFPS-b-PMMA, TFOS-b-PMMA and HFDS-b-PMMA) were mixed with PMMA in given compositions, respectively, and dissolved in chloroform. The resulting solutions were cast onto clean glass dishes to prepare films. The film appearance for the block copolymers and their PMMA blends was varied from transparent to opaque. Notably, the films of PDMS(9800)-b-PMMA, TFOS-b-PMMA, HFDS-b-PMMA and their PMMA blends were opaque, indicating the presence of phase separation, while TFPS-b-PMMA and their PMMA blend films were transparent.

Both the air- and glass-side surfaces were analyzed by ESCA in detail. Also, the contact angle and 180° peel strength were measured to correlate with their surface structures.

TABLE I

Synthesis of Poly(azo-containing siloxaneamide)s Having Fluoroalkyl Side Chains[a]

	Reactants										Product (PASA)						
Run no.	ACPC		BAS						Et$_3$N		CHCl$_3$	Yield		GPC			Appearance	Notation
	(g)	(mmol)	Rt[b]	Mn	m	n	(g)	(mmol)	(g)	(mmol)	(mL)	(g)	(%)	Mn	Mw	Mw/Mn		
Y-99	3.17	10	TFP	1200	0	7	12.00	10	2.02	20	20	13.99	92	10000	21000	2.01	Pale yellow viscous oil	PASA-TFP (1200)
7[c]	0.89	2.8	TFP	2500	0	14	7.00	2.8	0.57	5.6	40	6.53	85	12000	18000	1.50	Pale yellow viscous oil	PASA-TFP (2500)
Y-101	0.32	1	TFO	8200	59[d]	9[d]	8.20	1	0.20	2	20	7.71	91	27000	91000	3.37	Rubbery mass	PASA-TFO
Y-102	0.32	1	HFD	8400	49[d]	9[d]	8.40	1	0.20	2	20	7.15	82	44000	220000	5.03	Rubbery mass	PASA-HFD

[a] Mixed at 0–5°C over 30–40 min, followed by reaction at 17–20°C for 1 h, and then at 30°C for 1 h.
[b] TFP CH$_2$CH$_2$CF$_3$; TFO CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$; HFD CH$_2$CH$_2$(CF$_2$)$_7$CF$_3$.
[c] Lit. 9.
[d] Estimated from ^{1}H-NMR spectra.

TABLE II
Polymerization of MMA with Fluoroalkyl-Containing PASAs[a]

| Run no. | PASA | | | MMA (mmol) | Solvent[b] | (ml) | Temp. (°C) | Time (hr) | Yield (%) | Extraction residue[c] (%) | Siloxane content (wt %) | Polymer | | | Notation |
| | Rf | SCL (MW) | Azo (mmol) | | | | | | | | | GPC | | | |
												Mn ($\times 10^3$)	Mw ($\times 10^3$)	Mw/Mn	
Y-111	TFP	1200	3.3	200	MEK	20	80	3	81	100	6.3	33	62	1.87	TFPS (1200)-b-PMMA
M-16	TFP	2500	1.1	250	Tol	20	80	5	45	100	7.7	39	84	2.15	TFPS (2500)-b-PMMA
Y-105	TFO	8200	0.5	200	MEK	20	80	5	74	97	18.7	37	130	3.43	TFOS-b-PMMA
Y-109	HFD	8400	0.5	200	THF	20	60	8	80	99	18.5	49	800	16.5	HFDS-b-PMMA

[a] N₂ atmosphere.
[b] MEK methyl ethyl ketone; Tol toluene; THF tetrahydrofuran.
[c] Petroleum-ether insoluble fraction.
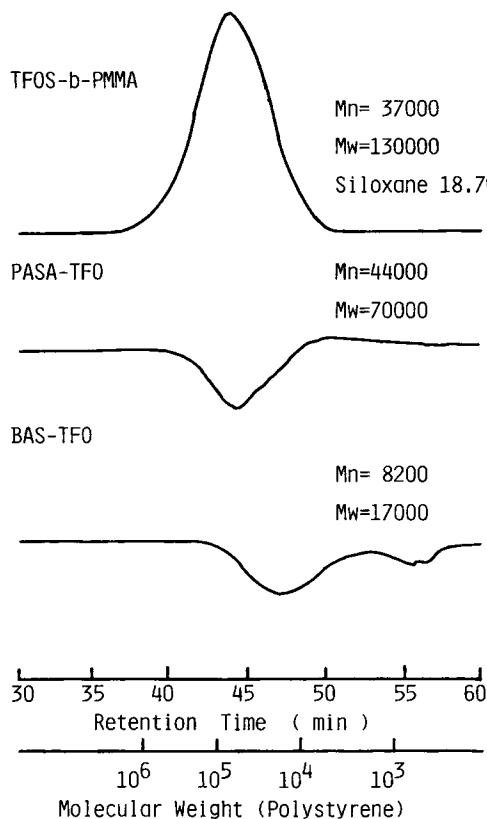
Fig. 1.   GPC curves of BAS-TFO, PASA-TFO and TFOS-b-PMMA.

Contact Angles of Solution-Cast Films

Figure 2 shows water contact angles of films of TFOS-b-PMMA, HFDS-b-PMMA and their PMMA blends, which have relatively long SCL and also long fluoroalkyl side chains, with reference to those of PDMS(9800)-b-PMMA.

It was confirmed that the water contact angles of the air-side surfaces for these blend systems were higher than those of the glass-side surfaces over a range of relatively low siloxane bulk concentration (i.e., siloxane content, as reported previously[1,2]). An abrupt increase of the contact angles on the air-side surfaces was also noted. The surface accumulation of siloxane segments were promoted by incorporation of long fluoroalkyl side chains, TFO, and HFD. Therefore, this phenomena was explained in terms of the promoted phase separation between siloxane segments and PMMA segments. The PMMA segments were confirmed to be almost compatible with PMMA homopolymers, as revealed from a single Tg for PMMA around 100°C by differential scanning calorimetry (DSC).

The critical surface tension (γ_c) data also exhibited very low energy surfaces, particularly, on their air-sides for TFOS-b-PMMA and HFDS-b-PMMA. Zisman plots of their air-side surfaces using hydric liquids, as shown in Figure 3, provided very low values, 11 and 9 dyne/cm for TFOS-b-PMMA and HFDS-b-PMMA, respectively.
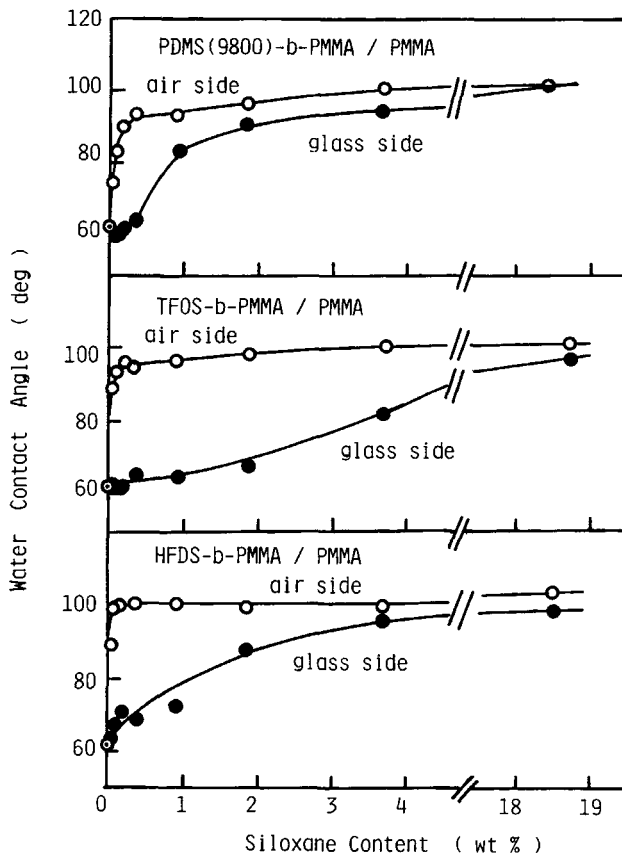
Fig. 2. Relationship between water contact angle and siloxane content for PDMS(9800)-b-PMMA/PMMA, TFOS-b-PMMA/PMMA and HFDS-b-PMMA/PMMA blend films.

The critical surface tensions of polymers having relatively long perfluoroalkyl side chains were summarized in Table III.

As can be seen from Table III, the low critical surface tensions of TFOS-b-PMMA and HFDS-b-PMMA are attributed to long fluoroalkyl side chains. Even hydrophilic poly(vinyl alcohol) films were reported to be modified by perfluorocarbonyl chlorides to afford low energy surfaces.[18] The surface models based on the critical surface tensions were proposed that the perfluoroalkyl chains vertically oriented on their surfaces in close packing.[13] In addition, poralization specular infrared spectra indicated that the fluoroalkyl side chains were approximately parallel to one another and normal to the substrate surface.[20]

Accordingly, the low critical surface tensions of TFOS-b-PMMA and HFDS-b-PMMA films similarly suggest the surface occupation of the long fluoroalkyl side chains, TFO and HFD in preference to siloxane chains. Furthermore, HFD group was confirmed to have more significant effect on decreasing the surface energy than TFO.

On the contrary, 3,3,3-trifluoropropyl (TFP) group did not show marked increase of hydrophobicity in TFPS(2500)-b-PMMA/PMMA blends, as revealed from slow increase of water contact angles with siloxane content and
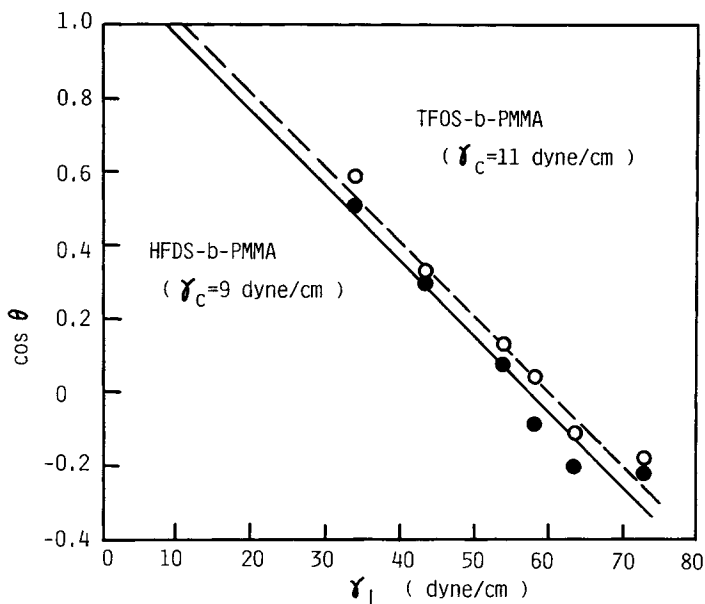
Fig. 3.   Zisman plots of air-side surfaces for TFOS-b-PMMA and HFDS-b-PMMA films.

small difference of contact angles between air-side and glass-side surfaces (Figure 4). Low hydrophobicity of TFPS(2500)-b-PMMA is probably due to good miscibility between siloxane segments and PMMA segments, because of polar nature of TFP group. Furthermore, it should be emphasized that the SCL for TFPS(2500)-b-PMMA was estimated to be 2500, corresponding to n = 14, shown in eq. (1). This n value is lower than the critical n value for phase separation, ca. 25 for SCL 2100 of PDMS-b-PMMA.[2] This is also quite lower than those of PDMS(9800)-b-PMMA, TFOS-b-PMMA and HFDS-b-PMMA.

Owen reported that the critical surface tensions of poly(trifluoropropylmethylsiloxane) (PTFPMS) was similar to that of PDMS, while the liquid surface tension of PTEPMS was higher than that of PDMS.[21] It is, therefore, noteworthy that the surface behavior of TFPS(2500)-b-PMMA/PMMA systems somewhat differs from that of PTFPMS. The increase of fluoroalkyl chain length, this is, PDMS-b-PMMA, TFPS-b-PMMA, TFOS-b-PMMA and HFDS-b-PMMA in the order, would be expected to increase the surface hydrophobicity. However, TFPS-b-PMMA did not fit into this simple pattern. TFPS-b-PMMA used here was speculated to form a homogeneous phase between TFPS segments and PMMA segments, differing from the other block copolymers, probably because of the low n-value and the polar nature of TFP group.

Thus, preferential surface accumulation of siloxane segments was observed for the block copolymers having long SCL and also relatively long fluoroalkyl chain length.

ESCA Analysis of Solution-Cast Films

Figure 5 illustrates typical ESCA spectra for PASA-HFD and, HFDS-b-PMMA and its PMMA blends on air-side surfaces.

Polymer	Critical surface tension (γ_c) (dyne/cm)	Reference
Perfluorocaproic acid	8.6	12
Perfluorocaprylic acid	7.9	12
Perfluorocapric acid	6.1	12
17-(perfluoroheptyl)-heptadecanoic acid	8.0	13
Poly(pentadecafluoro-1,1-dihydrooctyl acrylate)	10.4	14
Poly(pentadecafluoro-1,1-dihydrooctyl methacrylate)	10.6	15
Poly[2-(N-ethyl-N-heptadecafluorooctylsulfonyl)-aminoethyl acrylate	10.7–11.1	16
Poly[2-(N-propyl-N-heptadecafluorooctylsulfonyl)-aminoethyl acrylate	11.0	15
	11.7–12.1	16
Poly[2-(N-methyl-N-heptadecafluorooctylsulfonyl)-aminoethyl methacrylate	10.1	16
Poly[2-(N-ethyl-N-heptadecafluorooctylsulfonyl)-aminoethyl methacrylate	11.7	16
Poly(pentadecafluorooctadecanoyliminoethylene)	11	17
Perfluoroheptanoate of polyvinyl alcohol	15.8	18
Perfluorononanoate of polyvinyl alcohol	12.8	18
Hydrolyzate of 3-(pentadecafluoro-1,1-dihydrooctyl)propyl triethoxysilane	14	19
Poly[methyl(tridecafluoro-1,1,2,2-tetrahydrooctyl)siloxane]	11.9	20
Poly[methyl(heptadecafluoro-1,1,2,2-tetrahydrodecyl)siloxane]	18.3	20
TFOS-b-PMMA (air side)	11	this work
HFDS-b-PMMA (air side)	9	this work

It is noticed that no other element was detected except for F, O, C, and Si elements in ESCA spectra of PASA-TFO, PASA-HFD, and both the air- and glass-side surfaces for TFOS-b-PMMA, HFDS-b-PMMA and their PMMA blends. As the siloxane content increases, abrupt increase of F_{1s} and Si_{2p} peaks were observed in a relatively low level of siloxane content, eventually, less than 0.1 wt %. Moreover, C_{1s} peak patterns varied significantly with the siloxane content, indicating the appearance of TFO and HFD carbons on their surfaces. The top spectra in Fig. 5 show these peaks for the polyazoinitiator, PASA-
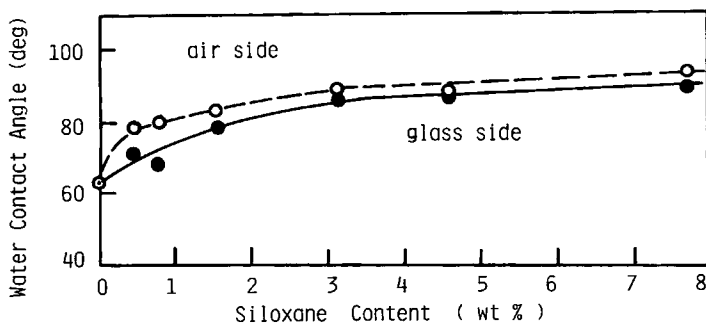

Fig. 4. Relationship between water contact angle and siloxane content for TFPS(2500)-b-PMMA/PMMA blend films.
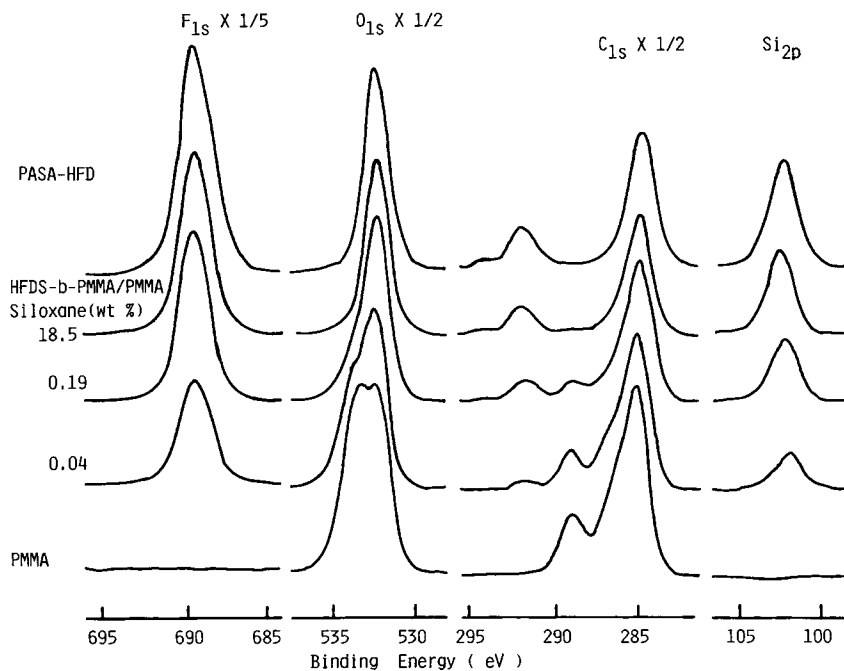

Fig. 5.   ESCA spectra of air-side surface of PASA-HFD, and HFDS-b-PMMA/PMMA blend films.

HFD, taken as liquid films, suggesting similar spectral pattern to those for HFDS-b-PMMA (siloxane content, 18.5 wt %). Peak intensity ratios, F_{1s}/C_{1s} and Si_{2p}/C_{1s} for neat block copolymers, corrected with photoelectron cross-section were much larger than those calculated for PASA-TFO and PASA-HFD, respectively, while O_{1s}/C_{1s} values were almost equal to the calculated ones. This implies the orientation of the fluoroalkyl siloxane chains to the air-side surfaces.

TABLE IV
ESCA Peak Assignment and Relative Peak Areas[a] of C_{1s} Core Levels for PASA-TFO, PASA-HFD, TFOS-b-PMMA (Air-Side), and HFDS-b-PMMA (Air-Side)[b]

Sample	CF_3	CF_2	CONH CN COO	CH_2NH CH_2CF_2 CH_3O CH_2CONH	$SiCH_2$ $SiCH_3$ CH_2-C (CH_3)
					(%)
PASA-TFO	2.8	15.3	1.2	9.4	71.3
	(294.4)	(292.1)	(289.4)	(269.8)	(285.0)
TFOS-b-PMMA	3.0	14.1	1.4	9.8	71.7
(air side)	(294.5)	(292.1)	(289.1)	(286.7)	(285.0)
PASA-HFD	2.5	21.0	1.1	6.1	69.3
	(294.6)	(292.2)	(289.5)	(287.1)	(285.0)
HFDS-b-PMMA	2.6	17.5	4.4	9.2	66.3
(air side)	(294.3)	(292.1)	(289.1)	(286.8)	(285.0)

[a] Curve resolution of C_{1s} peaks was based on Gaussian distribution.
[b] Values in parentheses represent binding energies in eV.

The detailed ESCA spectra of C_{1s} core levels for PASA-TFO, PASA-HFD, TFOS-b-PMMA (air-side) and HFDS-b-PMMA (air-side) are shown in Figure 6. The peak assignments were done by reference to the Clark's work.[22] The results of curve resolutions of C_{1s} peaks were listed in Table IV.

It was suggested that ESCA C_{1s} spectra of the air-side surfaces for TFOS-b-PMMA and HFDS-b-PMMA resembled those for the liquid films of PASA-b-TFO and PASA-b-HFD, respectively. This means that the surfaces of the neat block copolymer films were dominated by the PASA moieties, particularly, the siloxane segments. From this table, the peak intensity ratios, CF_2/CF_3 were estimated to be 4.7 and 6.7 for TFOS-b-PMMA and HFDS-b-PMMA, respectively, almost corresponding to the theoretical ones, 5 and 7, respectively, or slightly less. Not only methylsiloxane main chain but also TFO and HFO side chains were detected on the air-side surfaces within ESCA measuring depth (at most 20 Å). Therefore, TFO and HFD side chains inclined to the surface planes were speculated as the air-side surface structures, rather than those normal to the surface planes.
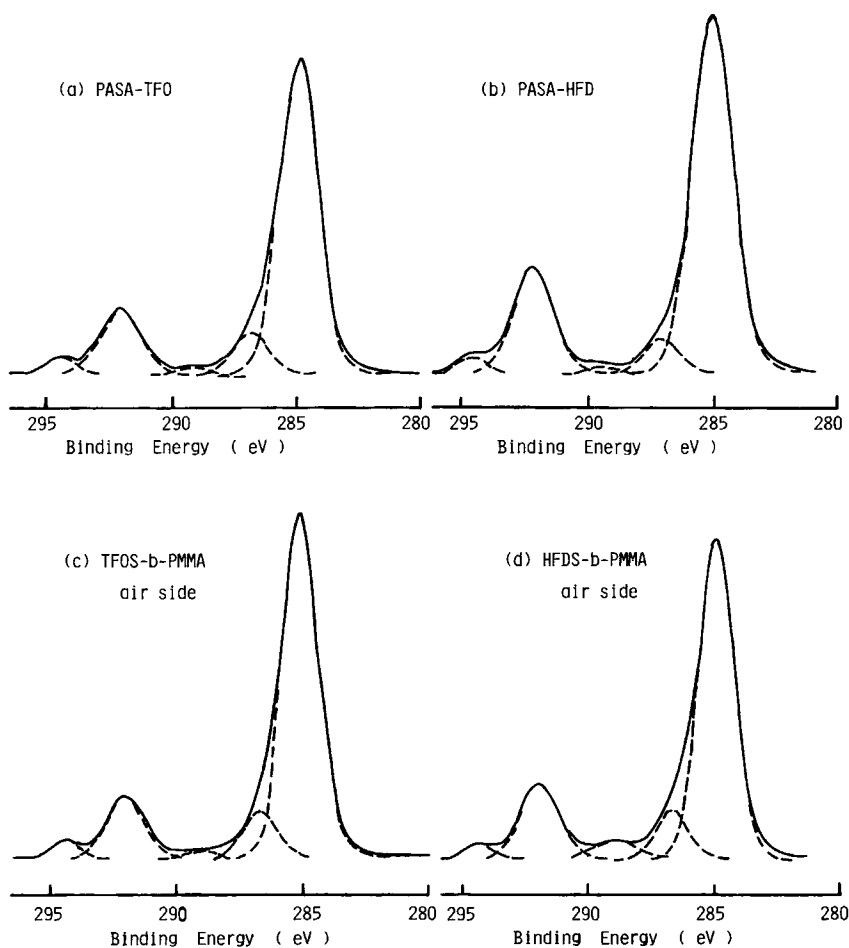

Fig. 6.   ESCA C_{1s} spectra for PASA-TFO(a), PASA-HFD(b), and air-side surfaces of TFOS-b-PMMA(c) and HFDS-b-PMMA(d).
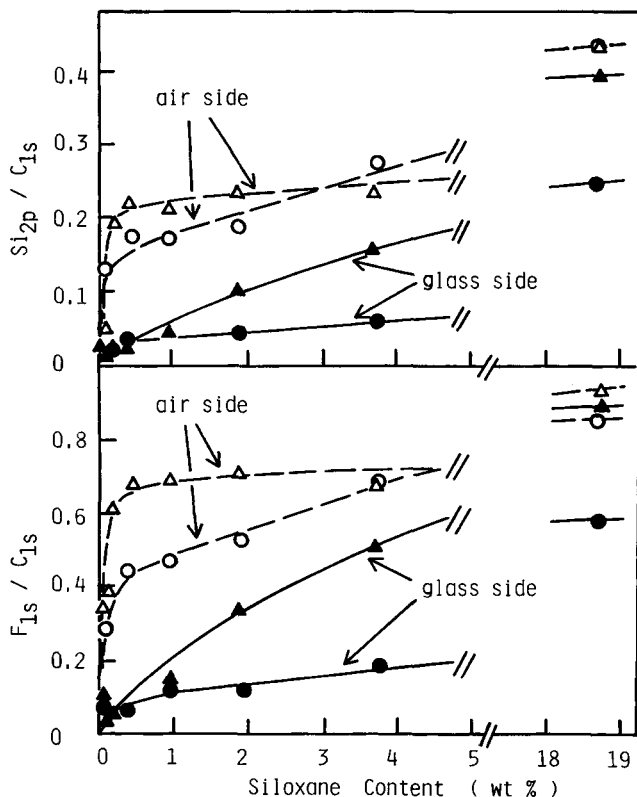
Fig. 7.   Dependence of siloxane content on ESCA F_{1s}/C_{1s} and Si_{2p}/C_{1s} ratios for TFOS-b-PMMA/PMMA and HFDS-b-PMMA/PMMA blend films.

	TFOS-b-PMMA/PMMA	HFDS-b-PMMA/PMMA
air side	—○—	—△—
glass side	—●—	—▲—

Figure 7 illustrates the plots of ESCA peak intensity ratios, F_{1s}/C_{1s} and Si_{2p}/C_{1s}, against siloxane contents for TFOS-b-PMMA/PMMA and HFDS-b-PMMA blend films.

It was found that the presence of both Si and F atoms greatly increased on the air-side surfaces with an increase of siloxane content. Particularly, in the case of HFDS-b-PMMA/PMMA system, both of Si_{2p}/C_{1s} and F_{1s}/C_{1s} peak ratios reached almost constant values within very low siloxane contents (less than 0.5 wt %), while on the glass-side surfaces Si and F atoms gradually increased. The shortening of the difluorocarbon unit, CF_2, leads to slightly lower increase in Si and F atoms on the surfaces, as can be seen from comparison between HFDS-b-PMMA and TFOS-b-PMMA. This also probed higher hydrophobic nature of HFD group than TFO group.

Conversely, TFP group was found to be classified into polar group rather than nonpolar hydrophobic one based on ESCA analysis and the above-mentioned contact angle data. Figure 8 shows ESCA spectra of the air- and glass-side surfaces for TFPS(2500)-b-PMMA blend films.
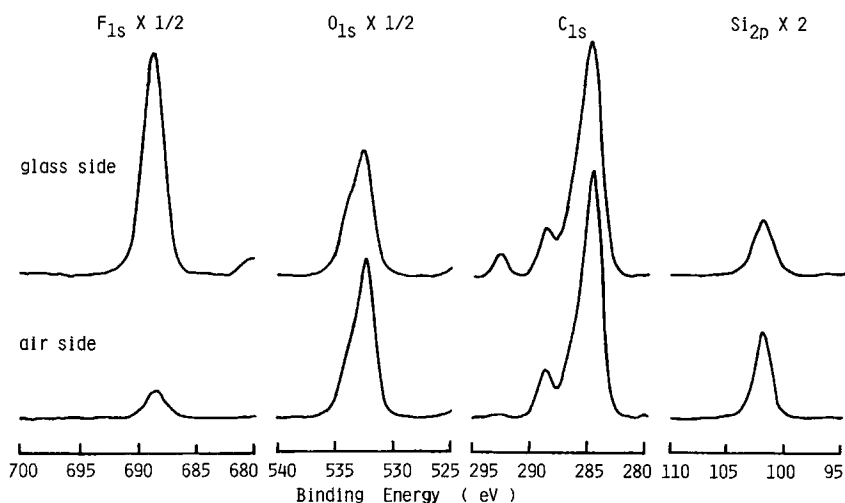
F_{1s} X 1/2 O_{1s} X 1/2 C_{1s} Si_{2p} X 2

glass side

air side

700   695   690   685   680 540   535   530   525 295   290   285   280 110   105   100   95

Binding   Energy   (eV)

Fig. 8.   ESCA spectra of air- and glass-side surfaces for TFPS(2500)-b-PMMA film.

In the air-side surface, the spectra were characterized by a low F_{1s} peak in spite of a relatively high Si_{2p} peak. This means that TFP group preferentially orients to the glass-side surface and to the inside of the films while methylsiloxane group orients to the air-side surface. The curve resolution of C_{1s} peaks clearly shows very low concentration of CF_3 group (at 293.0 eV) on the air-side surface as compared with that on the glass-side surface (see Figure 9).

Figure 10 illustrates plots of ESCA peak intensity ratios, F_{1s}/C_{1s} and Si_{2p}/C_{1s}, against siloxane content for TFPS(2500)-b-PMMA/PMMA blend films.

This figure evidently indicates that on the air-side surface the siloxane concentration gradually increased, while F_{1s}/C_{1s} ratios were held almost constant
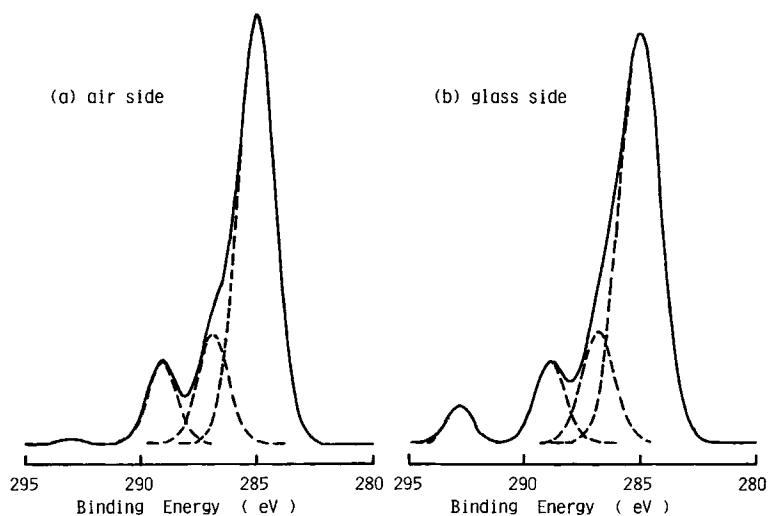
(a) air side   (b) glass side

295   290   285   280 295   290   285   280

Binding   Energy   (eV)   Binding   Energy   (eV)

Fig. 9.   ESCA C_{1s} spectra of air(a)- and glass-side surfaces(b) for TFPS(2500)-b-PMMA film.
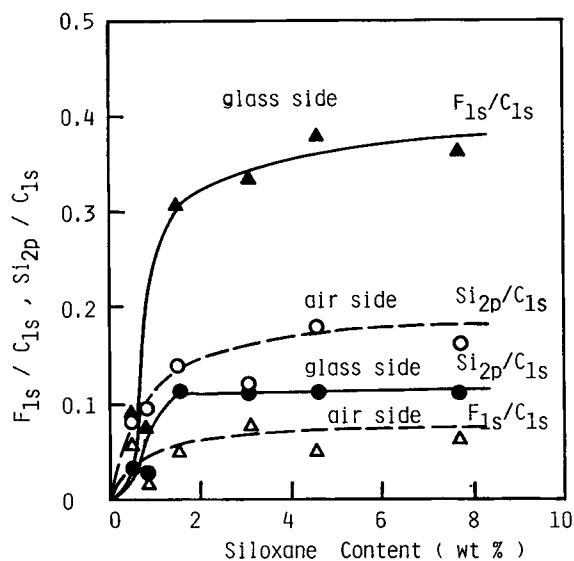
Fig. 10.   Dependence of siloxane content on ESCA F_{1s}/C_{1s} and Si_{2p}/C_{1s} ratios for TFPS (2500)-b-PMMA/PMMA blend films.

	Si_{2p}/C_{1s}	F_{1s}/C_{1s}
air side	—○—	—△—
glass side	—●—	—▲—

at low values. On the glass-side surfaces, conversely, it is noted that Si_{2p}/C_{1s} ratios were low and almost constant while F_{1s}/C_{1s} ratios were approximately three times higher than Si_{2p}/C_{1s} ratios. It may be, therefore, speculated for TFPS-b-PMMA/PMMA blend films that only the methylsiloxane group orients to the air-side surfaces, but TFP group is oriented to the inside of the films. Conversely, both of the methylsiloxane and TFP groups were presumed to orient to the glass-side surfaces. This structural speculation was examined by rough estimation of surface concentrations of the functional groups (i.e., $-(CH_3)SiO-$, $-CH_2CH_2CF_3$ (TFP), $-CH_2-C(CH_3)-$ and $-COOCH_3$) from F_{1s}/C_{1s}, O_{1s}/C_{1s}, and Si_{2p}/C_{1s} values assuming the simple bulk structures of block copolymers, as shown in eq. (2).

$$\left(\!\begin{array}{c} CH_3 \\ | \\ SiO\!-\!\!-\!\!- \\ | \\ CH_2CH_2CF_3 \end{array}\!\right)_{\!\!x}\!\!\left(\!\begin{array}{c} CH_3 \\ | \\ CH_2\!-\!C\!\!-\!\!- \\ | \\ COOCH_3 \end{array}\!\right)_{\!\!100-x} \qquad (2)$$
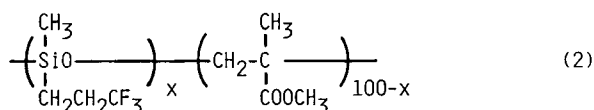
Figure 11 shows the calculated group surface concentrations of the functional groups plotted as a function of siloxane content for TFPS(2500)-b-PMMA blend films.
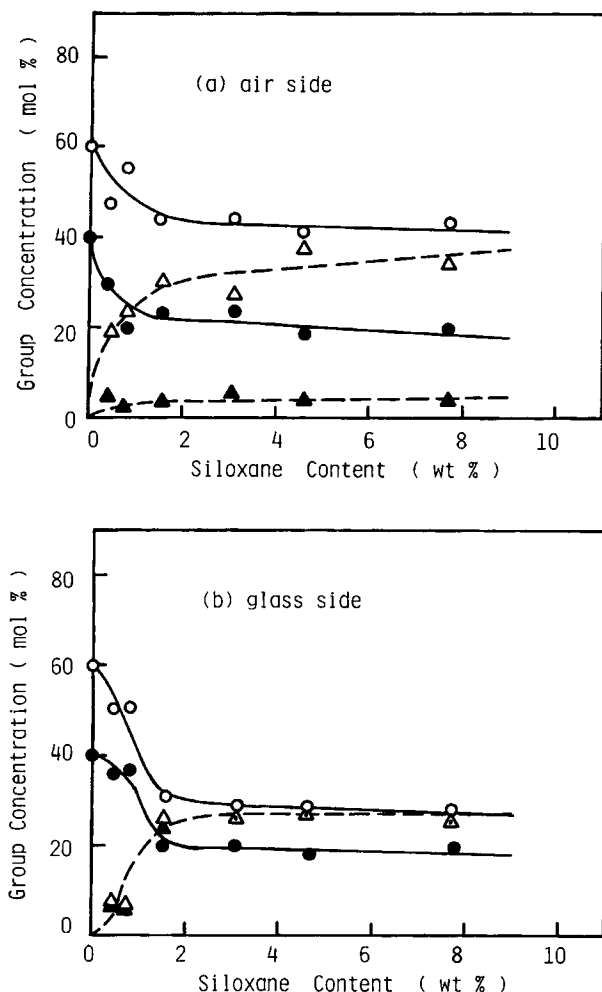
Fig. 11. Relationship between group surface concentration and siloxane content on (a) air- and glass-side surfaces (b) for TFPS(2500)-b-PMMA/PMMA blend films: —O— —CH$_2$C(CH$_3$)—; —●— —COOCH$_3$; —△— —Si(CH$_3$)O—; —▲— —CH$_2$CH$_2$CF$_3$.

On the air-side surfaces, the methylsiloxane and TFP groups concentration increased with siloxane content. However, the increase of the TFP group concentration was very gradual, leading to a significant difference in concentration with the methylsiloxane group concentration. On the glass-side surfaces, both of the methylsiloxane and TFP groups have almost same surface concentrations, and their group concentrations slowly increase. These results confirm the reverse orientation of the methylsiloxane and TFP groups on the air-side surface, in spite of the same-directional orientation of both the groups on the glass-side surfaces.

This ESCA data suggest that TFP group with relatively low SCL ($n = 14$) functions as a polar side chain because of CH$_2$CH$_2$CF$_3$ dipole. TFP siloxane
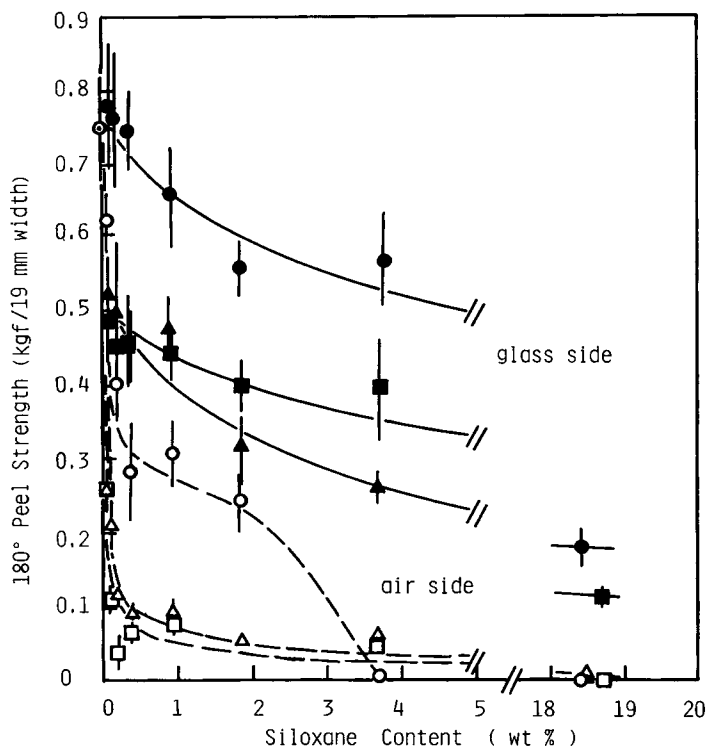
Fig. 12.   Relationship between 180° peel strength and siloxane content for PDMS(9800)-b-PMMA/PMMA, TFOS-b-PMMA/PMMA and HFDS-b-PMMA/PMMA blend films.

Polymer system	Air side	Glass side
PDSM(9800)-b-PMMA/PMMA	—○—	—●—
TFOS-b-PMMA/PMMA	—□—	—■—
HFDS-b-PMMA/PMMA	—△—	—▲—

segments (TFPS) were, therefore, miscible with PMMA segments to afford transparent films.

ESCA analysis of the crosslinked poly(trifluoropropylmethylsiloxane), as reported by Owen,[23] indicated somewhat higher fluorine content on its surface than the theoretical one. However, the trifluoroacetate moiety were preferentially oriented into the bulk of trifluoroacetylated methyl methacrylate-hydroxypropyl methacrylate copolymers away from the surface, as evidenced by ESCA analysis.[24] These results given in the literatures may suggest that the CF_3 bond polarity plays important role to control their surface structure, depending on copolymers and sequence length.

The surface behavior of TFPS-b-PMMA blend films was quite different than that of long fluoroalkyl side chains (i.e., TFO and HFD), which were more accumulated on the air-side surfaces. The surface accumulation of meth-
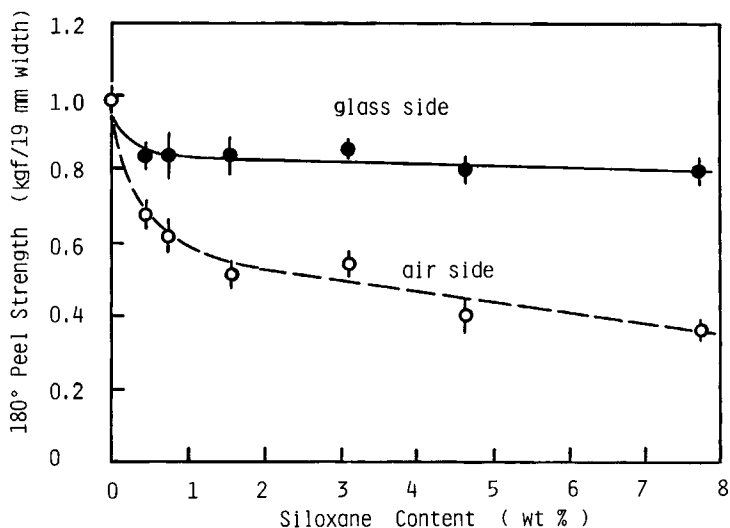
Fig. 13. Relationship between 180° peel strength and siloxane content for TFP(2500)-b-PMMA/PMMA blend films.

ylsiloxane and fluoroalkyl groups will reflect on adhesion performance of their films surfaces as adherends.

Adhesion Performance of Film Surfaces

The adhesion of the film surfaces toward pressure-sensitive adhesion tapes was taken as a measure of adhesion performance. Figure 12 shows the 180° peel strength of PDMS(9800)-b-PMMA, TFOS-b-PMMA, HFDS-b-PMMA and their PMMA blends toward pressure-sensitive adhesive tapes.

On the air-side surface, it was found that the peel strength abruptly decreased with an increase of siloxane content. Both of TFOS-b-PMMA and HFDS-b-PMMA systems exhibited more significant effect on the release property than PDMS(9800)-b-PMMA systems. The difference between TFO and HFD side chain was not clear from these peel data of the air-side surfaces, but the glass-side surfaces for HFDS-b-PMMA/PMMA systems revealed higher hydrophobicity than those for TFOS-b-PMMA/PMMA systems. In TFOS-b-PMMA and HFDS-b-PMMA and their polymer blends, both of the methylsiloxane and fluoroalkyl groups oriented to the topmost surfaces were proved to be an origin of excellent release property or repellency.

In Figure 13, the 180° peel strength is plotted as a function of siloxane content for TFPS(2500)-b-PMMA/PMMA blend films. Slight decrease of the peel strength was observed on the glass- and air-side surfaces in the region of low siloxane contents, in contrast to those of HFDS-b-PMMA and TFOS-b-PMMA systems shown in Fig. 12. This is attributed to relatively low surface accumulation of TFPS chains and also its higher surface energy. More decrease of the peel strength on the air-side surfaces than that on the glass-side surfaces obviously indicates that the methylsiloxane groups more oriented to the air-
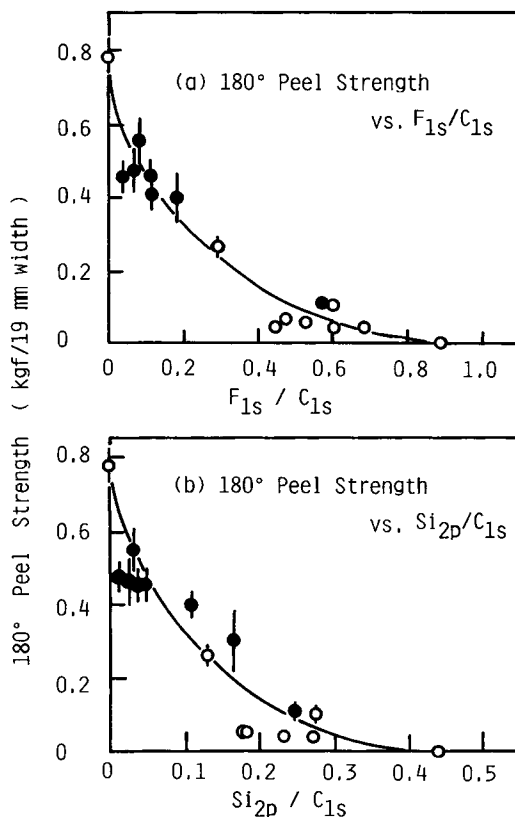
Fig. 14. Dependence of ESCA F_{1s}/C_{1s} and Si_{2p}/C_{1s} ratio on 180° peel strength for TFOS-b-PMMA/PMMA blend films: —O— air side; —●— glass side.

side surfaces functioned as moderate release agents, but on the other hand, TFP side chains and PMMA segments oriented to the glass-side surfaces little exhibited release property.

Thus, the long fluoroalkyl side chains, TFO and HFD groups, were confirmed to be accumulated on the air-side surfaces for the block copolymer/PMMA blend films, in which the flexible siloxane chains were also preferentially surface-accumulated. These long fluoroalkyl side chains were very hydrophobic in contrast to TFP group, as evidenced by the critical surface tensions. Therefore, the adhesion performance or release property of those blend films is expected to be influenced by both of fluoroalkyl and siloxane surface concentrations.

Figure 14 illustrates the dependence of ESCA F_{1s}/C_{1s} and Si_{2p}/C_{1s} ratios on 180° peel strength for TFOS-b-PMMA/PMMA systems, as an example.

The peel strength decreased as both of the F_{1s}/C_{1s} and Si_{2p}/C_{1s} ratios increased. This suggests that surface accumulation of not only TFO side chains, but also the siloxane chains resulted in enhanced release activity. This phenomena were also observed in HFDS-b-PMMA/PMMA blend films.

In conclusion, surface structure of fluoroalkyl siloxane-PMMA block copolymers, in which the fluoroalkyl groups as side chains were linked to the flexible siloxane main chains, were influenced by fluoroalkyl chain length, si-

loxane chain length (SCL), siloxane content, and so on. In this work, particularly, effect of the fluoroalkyl groups and their chain length was intensively studied to obtain some information on surface segregation behavior of the fluoroalkyl siloxane segments, based on contact angle, ESCA and peel strength measurements.

It was found that the fluoroalkyl groups having relatively long chain length (i.e., TFO and HFD groups), themselves were phase-separated from PMMA segments and also enhanced the surface accumulation of methylsiloxane groups. In contrast to TFPS-b-PMMA/PMMA systems, TFOS-b-PMMA/PMMA and HFDS-b-PMMA/PMMA systems were observed to enhance release property, or repellency to adhesion, as a result of surface accumulation of the both the fluoroalkyl and methylsiloxane chains. These interesting phenomena imply useful application of fluoroalkylsilicone—vinyl block copolymers to surface modifiers, especially as release agents with excellent hydrophobicity and oleophobicity.

References

1. H. Inoue, A. Ueda, and S. Nagai, *J. Appl. Polym. Sci.*, **35**, 2039 (1988).

2. H. Inoue, A. Matsumoto, K. Matsukawa, A. Ueda, and S. Nagai, *J. Appl. Polym. Sci.*, submitted.

3. D. W. Dwight, J. E. McGrath, A. R. Beck, and J. S. Riffle, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **20**(1), 702 (1979).

4. J. E. McGrath, D. W. Dwight, J. S. Riffle, T. F. Davidson, D. C. Webster, and R. Viswanathan, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **20**(2), 525 (1979).

5. J. S. Riffle, Ph.D. Dissertation, V. P. I. & S. U., (1980).

6. D. W. Dwight and H. R. Thomas, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **23**, 302 (1981).

7. A. K. Shaaban, S. McCartney, N. Patel, I. Yilgör, J. S. Riffle, D. W. Dwight, and J. E. McGrath, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **24**(2), 130 (1983).

8. N. M. Patel, D. W. Dwight, J. L. Hedrick, D. C. Webster, and J. E. McGrath, *Macromolecules*, **21**, 2689 (1988).

9. H. Inoue, A. Ueda, and S. Nagai, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 1077 (1988).

10. J. S. Riffle, I. Yilgor, C. Tran, G. L. Wikes, J. E. McGrath, and A. K. Banthia, *Epoxy Resin Chemistry II*, ed. by R. S. Bauer, ACS Symposium Ser. 221, p. 21 (1983).

11. Y. Kitazaki and T. Hata, *J. Adhesion Soc. Jpn.*, **8**, 131 (1972).

12. E. F. Hare, E. G. Shafrin, and W. A. Zisman, *J. Phys. Chem.*, **58**, 236 (1954).

13. E. G. Shafrin and W. A. Zisman, *J. Phys. Chem.*, **66**, 740 (1962).

14. A. G. Pittman, D. L. Sharp, and B. A. Ludwig, *J. Polym. Sci.* A-1, **6**, 1729 (1968).

15. M. K. Bernett and W. A. Zisman, *J. Phys. Chem.*, **66**, 1207 (1962).

16. R. Ramharack and T. H. Nguyen, *J. Polym. Sci. C, Polym. Lett.*, **25**, 93 (1987).

17. M. Litt and J. Herz, *J. Colloid Interface Sci.*, **31**, 248 (1969).

18. K. Ogino, T. Ohtsuka, and N. Ishikawa, *Kobunshi Ronbunshu*, **43**, 377 (1986).

19. W. D. Bascon, *J. Colloid Interface Sci.*, **27**, 789 (1968).

20. M. M. Doeff and E. Lindner, *Macromolecules*, **22**, 2951 (1989).

21. M. J. Owen, *Ind. Eng. Chem. Prod. Dev.*, **19**, 97 (1980).

22. D. T. Clark, *Pure Appl. Chem.*, **54**, 415 (1982).

23. M. J. Owen, *J. Appl. Polym. Sci.*, **35**, 895 (1988).

24. R. A. Dickie, J. S. Hammond, J. E. deVries, and J. W. Holubka, *Anal. Chem.*, **54**, 2045 (1982).