

Synthesis of Polysiloxane-Grafted Fluoropolymers and Their Hydrophobic Properties

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ABSTRACT: A polydimethylsiloxane with an epoxide end group was grafted onto a fluoropolymer that had hydroxyl side chains by using protonic or Lewis acids as catalysts. Strong acids such as trifluoromethanesulfonic acid were found to be effective for the grafting of the polydimethylsiloxane of relatively large molecular weight (M_n 4440). A coating prepared from the graft polymer was so hydrophobic that a water droplet of 10 μ L slid down on its inclined plane surface (30° with respect to the horizontal). ESCA analysis revealed that the siloxane branches are preferentially present on the surface. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1955–1963, 2000

Key words: fluoropolymer; polydimethylsiloxane; grafting; water-repellent; coating

INTRODUCTION

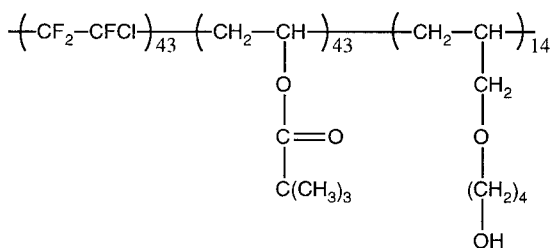
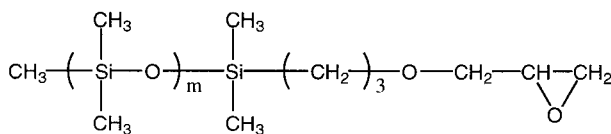
A variety of hydrophobic materials made of synthetic polymers have been investigated for practical uses. Thus far, fluoropolymers, represented by Teflon, have been used widely for such purposes because they have oil-repellent as well as water-repellent properties. On the other hand, polysiloxanes have also been investigated for development of their various applications. Water drops easily roll down on inclined plane surfaces of fluoropolymers because contact angles of water on the surfaces are rather large: around 110°. However, a small water droplet, of 10 μ L, remains on the surfaces even when it is vertical. This is ascribed to a polar interaction between water molecules and the highly polarized carbon–fluorine bonds of the fluoropolymers. Although water drops slide down easily on the inclined surface of solid polydimethylsiloxane, in spite of the relatively small contact angle, there are some prob-

lems in practical application of the polymer; for example, it lacks required mechanical properties such as hardness. Polysiloxanes that have fluorinated alkyl side chains have been synthesized to have a combination of the properties of fluoropolymers and polysiloxanes; they are expected to be developed for water-repellent materials.¹ Although the contact angles of water on them has been demonstrate, the sliding of water droplets on the coatings of such materials has not been discussed. Murase et al.² reported that the sliding of water droplets was enhanced on coatings prepared from a copolymer obtained by grafting an isocyanate-terminated polydimethylsiloxane onto a fluoropolymer with hydroxyl side chains. Improved water-sliding properties were observed on the coating of a copolymer grafted with the polysiloxane of longer chain length. However, it is usually difficult to graft such polysiloxanes onto fluoropolymers because of their poor miscibility.

In this study we grafted a polydimethylsiloxane that has an epoxide end group onto a fluoropolymer with hydroxyl side chains by using strong acids as catalysts. We then prepared coat-

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P1 (\overline{M}_n 12400)P2a (\overline{M}_n 1230)P2b (\overline{M}_n 2670)P2c (\overline{M}_n 4440)

Scheme 1

ings from the graft copolymers obtained in order to examine their hydrophobic properties.

EXPERIMENTAL

Materials

Central Grass Co. Ltd. provided a fluoropolymer with hydroxyl side chains (P1), whose structure is shown in Scheme 1: \overline{M}_n 12,400 (GPC), fluorine content 20 wt %, hydroxyl value 65 mg KOH/g. The structure of polydimethylsiloxane (P2), a commercial product of the Chisso Corp., is also displayed in Scheme 1: \overline{M}_n 1230 (P2a), 2670 (P2b), 4440 (P2c); these values were determined by epoxide analysis. *N,N,N'*-Tris(ω -isocyanatohexyl)-isocyanate, supplied by the Nippon Polyurethane Co., was used as a crosslinking agent for preparation of coatings (Coronate HX); it was used as received. Other special grade reagents and solvents were used without further purification.

Grafting Reaction

Prescribed amounts of P1, P2, toluene, and a magnetic stirring bar were placed in a flask equipped with a calcium chloride tube. The mixture was stirred for 10 min at room temperature

(23°C). The flask was purged with argon and kept in a bath thermostated at a reaction temperature, and then a certain amount of an acid catalyst was injected into the flask under argon with stirring. The grafting ratio was calculated on the basis of a decrease in the peak of polydimethylsiloxane in GPC spectra according to the following equation:

$$\text{grafting ratio (\%)} = \frac{\text{grafted P2}}{\text{fed P2}} \times 100$$

The calculation was performed by using a computer on the assumption that the overlapped GPC peak would be composed of Gaussian peaks of each polymer.

Preparation of P3 Coatings

A certain amount of the crosslinking agent (the isocyanate group was equimolar to the hydroxyl groups in P3) was added to a homogeneous toluene solution of P3 obtained by the grafting reaction at 40°C for 1 h. The solution was cast on a glass plate, and the plate was kept in a oven thermostated at 140°C for 30 min. The P3 coating formed on the glass plate was washed with acetone using an ultrasonic bath to remove unreacted free P2.

Measurements

Gel Permeation Chromatography (GPC)

GPC measurements were carried out on a JASCO GPC system that was composed of an HPLC pump (PU-980), an RI detector (830-RI), and a column oven (860-CO) equipped with a TSK gel column (G4000HHR). After grafting, the reaction solutions were diluted with THF as an eluent and injected into the GPC system.

Sliding Angles for Water Drops on P3 Coatings

The sliding angles for water drops on the surfaces of the coatings were measured by using a contact angle meter CA-X (Kyowa Interface Science Co., Ltd.) equipped with a tiltable sample stage. A water drop of a prescribed volume was deposited on a P3-coated glass plate that had been placed on the sample stage, which was initially in a horizontal position and then was tilted slowly (1°/sec) until the drop started to slide down. The tilting angle with respect to the horizontal was defined as a sliding angle (α) for the drop.

ESCA Analysis

ESCA analysis was performed on a SHIMADZU ESCA-1000 electron spectrometer equipped with a Mg-K α X-ray gun. Argon plasma was used to etch the surfaces of the coatings.

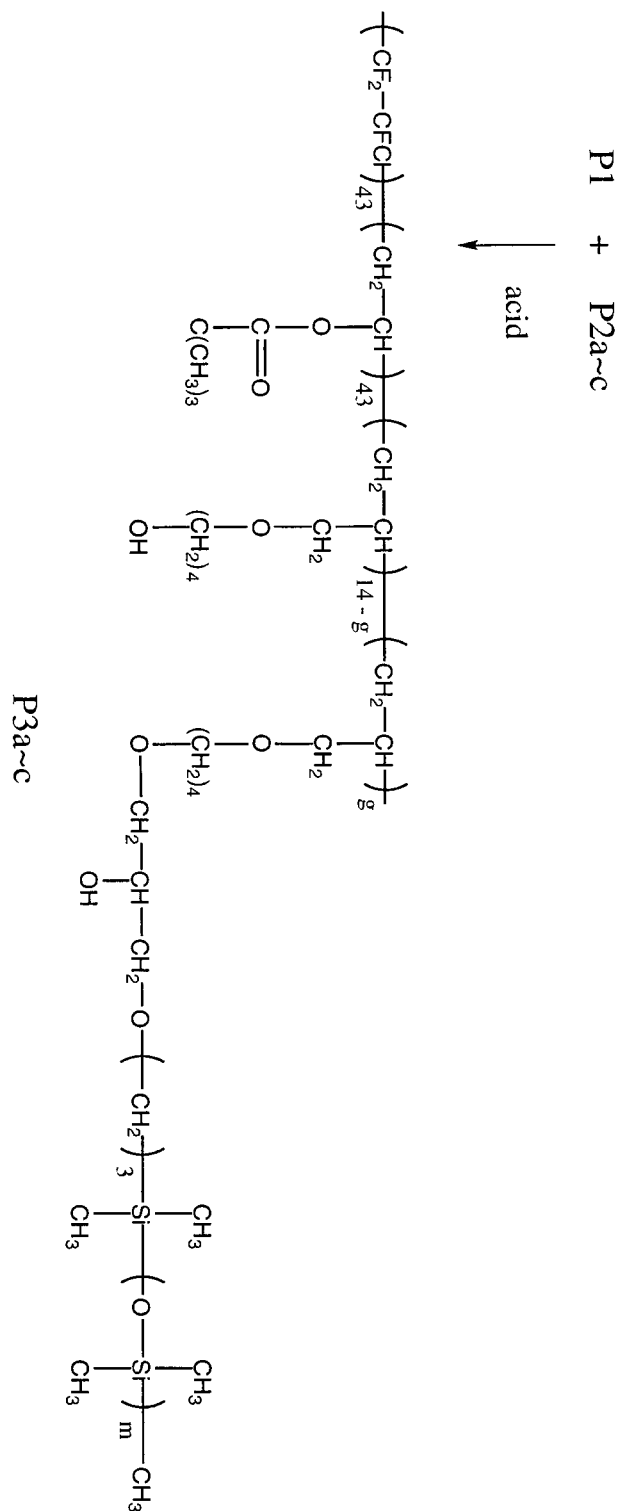
RESULTS AND DISCUSSION

Synthesis of Graft Polymers

P3 graft polymers (Scheme 2) were synthesized via the reaction of hydroxyl side groups of a P1 with the epoxide end group of a P2 by using various acid catalysts.

Figure 1 shows the change in the GPC spectra during the grafting reaction of P2a onto P1 catalyzed by stannic chloride. The peak of P2a decreased and the P1 peak sifted a little to the region of higher molecular weight with increasing reaction time. This indicates that the grafting reaction proceeded in the presence of the Lewis acid.

In the case of low molecular compounds, the ring-opening addition of an epoxide group to a hydroxyl group takes place easily in the presence of an acid catalyst. However, polymeric compounds require a lot of effective catalysts and/or a higher reaction temperature for such a reaction because their is considerable suppression of the reaction by their sterically hindering long chains. When polymers bearing hydroxyl side chains are kept with a strong acid at a high temperature, crosslinking sometimes occurs because intermolecular dehydration of the hydroxyl groups forms ether linkages between the polymer chains. Gelation of a P1 solution was actually observed after 2 h at 60°C in the presence of trifluoromethanesulfonic acid (TFMSA). A marked increase in the molecular weight of the polymer was observed on a GPC spectrum obtained with the reaction solution just before the gelation. This is indicative of the intermolecular dehydration between the hydroxyl groups of its side chains. On the other hand, when a weak acid such as acetic acid was used, neither the dehydrative crosslinking nor the grafting took place. To obtain the graft polymer by promoting the preferential reaction between the hydroxyl side groups of P1 and the epoxide end of P2, thereby suppressing the dehydration that causes crosslinking, various acid catalysts were examined. The results are shown in Table I. Grafting ratios were small when halogen-substituted acetic acids were used because their



Scheme 2

catalytic action is weak, even in the case of trifluoroacetic acid. A large grafting ratio was observed when TFMSA, a very strong acid, was

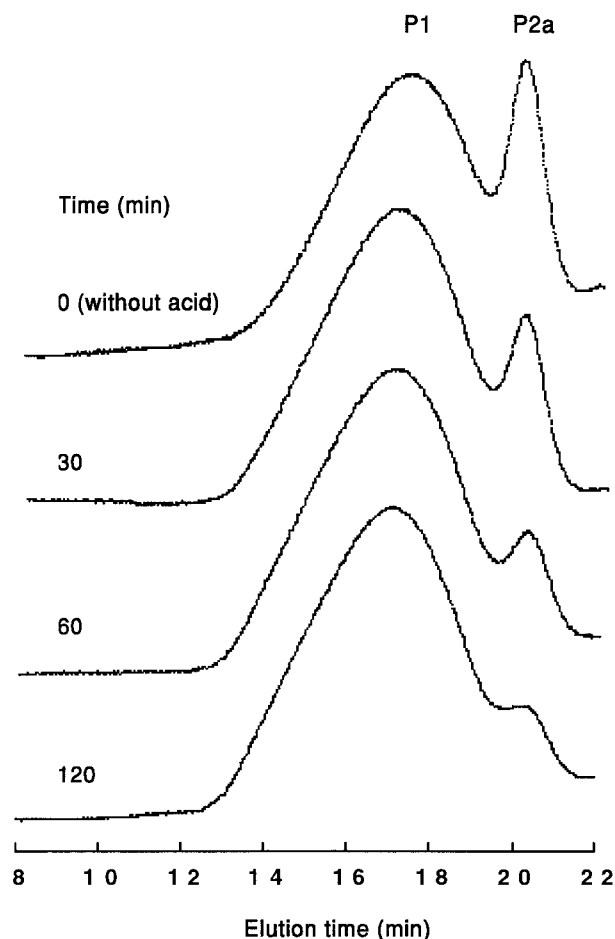


Figure 1 The change in GPC spectra during the graft reaction of P2a onto P1: P1 1.72 g (hydroxyl group 2 mmol), P2a (M_n 1230) 1.23 g (epoxide group 1 mmol), SnCl_4 52.1 mg (0.2 mmol), toluene 3.5 mL, 23°C.

used. Methyl trifluoromethanesulfonate acts as a carbocation catalyst, and its catalytic action in this reaction was quite a bit smaller than that of TFMSA. Trimethylsilyl trifluoromethanesulfonate was an effective catalyst, enabling the attainment of a large grafting ratio because of its distinguished catalysis of trimethylsilylation.³ Lewis acids such as stannic chloride and boron trifluoride were effective catalysts for this grafting reaction, and their catalytic effects were comparable to those of sulfonic acids and their derivatives.

Grafting ratios in the reactions catalyzed by various types of acids were plotted against reaction time (Fig. 2). When TFMSA was used as a strong protonic acid, the grafting proceeded fastest. In the reaction with methyl trifluoromethanesulfonate, the initial rate was relatively small, but the grafting ratio increased gradually with

increasing reaction time, eventually exceeding 80%.

The grafting reaction using TFMSA, which had shown a remarkable catalytic action, was further examined at elevated temperatures (Fig. 3). In the reaction at 60°C the grafting ratio exceeded 80% in 1 h; however, viscosity of the reaction solution increased because the dehydrative crosslinking of hydroxyl side groups occurs at higher reaction temperature, as described above, and gelation was observed after 2 h. At 40°C no gelation occurred after the grafting proceeded to a high ratio, above 80%, and no increase in viscosity of the reaction solution was observed. These results indicate that at this temperature grafting via the reaction between the hydroxyl side groups of the fluoropolymer and the epoxide end of the polydimethylsiloxane proceeded was predominant, in situations where the intermolecular dehydration of the hydroxyl groups leading to crosslinking was effectively suppressed.

Figure 4 shows the effect of TFMSA concentration on the grafting. The acid is immiscible with toluene; consequently, the reaction solution was turbid just after its addition because phase separation of its small droplets occurred. However, the solution became homogeneous and transparent after several minutes, indicating that the acid reacted with the polymers. The grafting ratio increased with an increasing concentration of the acid catalyst. Although the increased acid enhanced the rate of grafting, the increased residual acid in the reaction solution makes it difficult to prepare coatings from the solution because the remaining acid also accelerates the crosslinking of P3, in which hydroxyl groups react with the isocyanate crosslinking agent, shortening pot life of the solution for preparation of the coatings.

Table I Effect of Acidic Catalysts on Grafting^a

Acid Catalyst	Grafting Ratio (%)
CHCl_2COOH	10.8
CF_3COOH	12.0
$\text{CH}_3\text{SO}_3\text{H}$	25.8
$\text{CF}_3\text{SO}_3\text{H}$	72.8
$\text{CF}_3\text{SO}_3\text{CH}_3$	21.0
$\text{CF}_3\text{SO}_3\text{Si}(\text{CH}_3)_3$	68.9
SnCl_4	54.1
$\text{BF}_3\text{—O}(\text{C}_2\text{H}_5)_2$	36.5

^a Conditions: P1 1.72 g (hydroxyl group 2 mmol), P2a 0.62 g (epoxide group 0.5 mmol), an acid catalyst 0.1 mmol, toluene 3.5 mL; 23°C, 1 h.

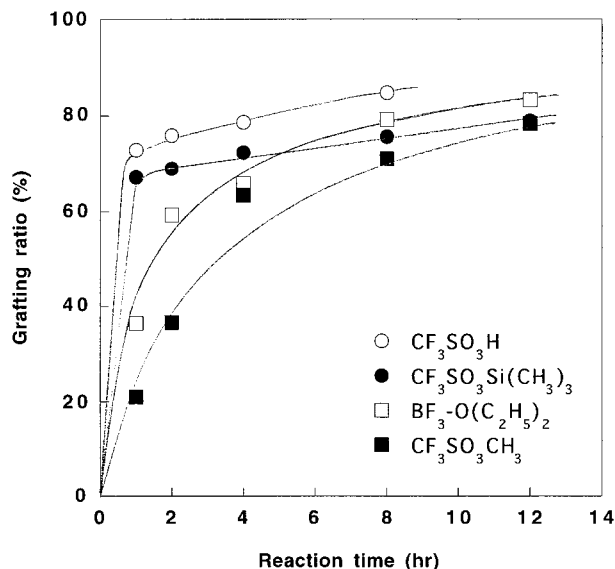


Figure 2 Plots of grafting ratios versus reaction time: P1 1.72 g (hydroxyl group 2 mmol), P2a 0.62 g (epoxide group 0.5 mmol), an acid catalyst (0.1 mmol), toluene 3.5 mL, 23°C.

The sliding of water droplets is facilitated on coating surfaces prepared from a P3 with longer polydimethylsiloxane branches.⁴ Accordingly, the grafting of P2s with different molecular weights (P2a, P2b, P2c) was examined. Although the grafting reaction of P2a, whose molecular weight

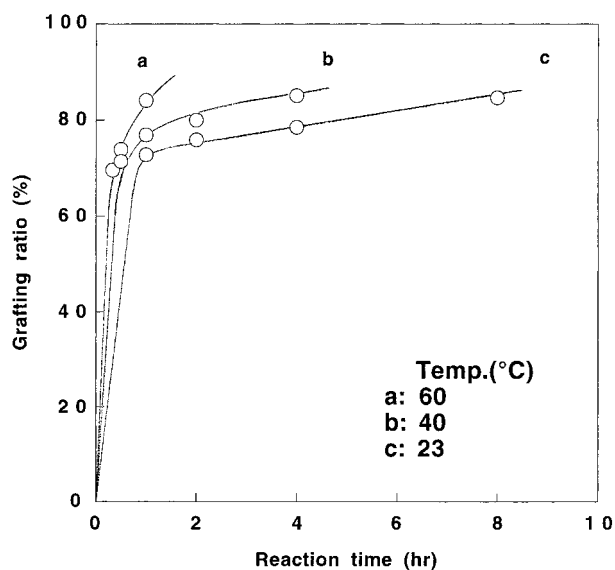


Figure 3 The grafting reaction catalyzed by TFMSA at various temperatures: P1 1.72 g (hydroxyl group 2 mmol), P2a 0.62 g (epoxide group 0.5 mmol), TFMSA 15.0 mg (0.1 mmol), toluene 3.5 mL.

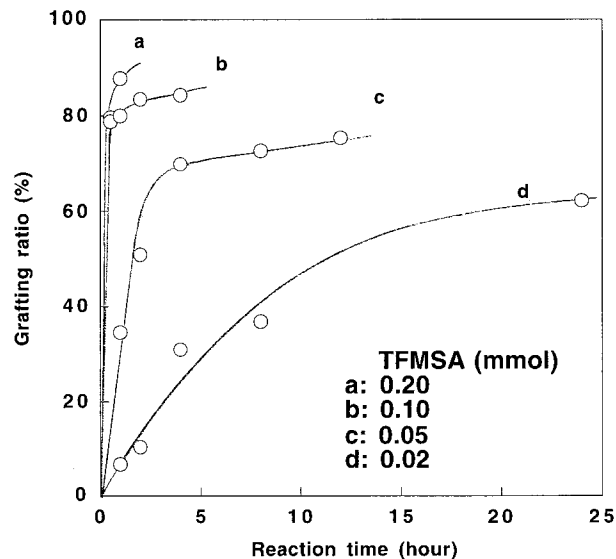


Figure 4 The effect of TFMSA concentration on grafting: P1 1.72 g (hydroxyl group 2 mmol), P2a 0.62 g (epoxide group 0.5 mmol), toluene 3.5 mL, 40°C.

is relatively small (M_n 1230), took place in the presence of methanesulfonic acid as a catalyst, this acid was not an effective catalyst for the grafting of P2c, which has a larger molecular weight (M_n 4440). As shown in Figure 5, when TFMSA was used as a catalyst, the grafting of

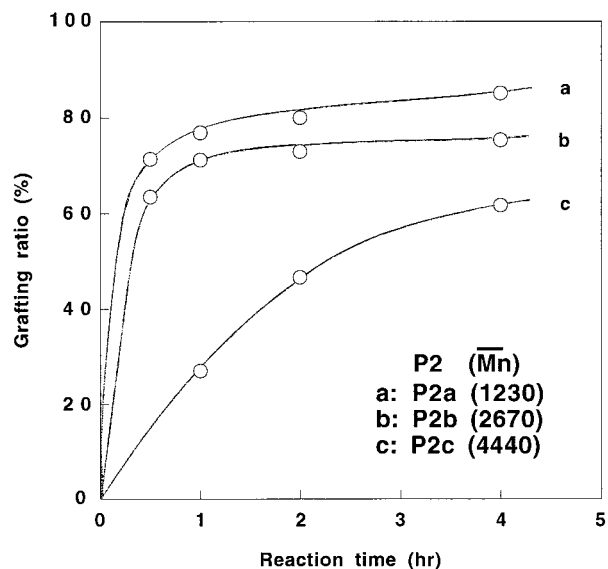


Figure 5 The effect of molecular weight of P2 on grafting: P1 1.72 g (hydroxyl group 2 mmol), P2a 0.62 g (epoxide group 0.5 mmol), P2b 1.34 g (epoxide group 0.5 mmol), P2c 2.22 g (epoxide group 0.5 mmol), TFMSA 15.0 mg (0.1 mmol), toluene 3.5 mL, 40°C.

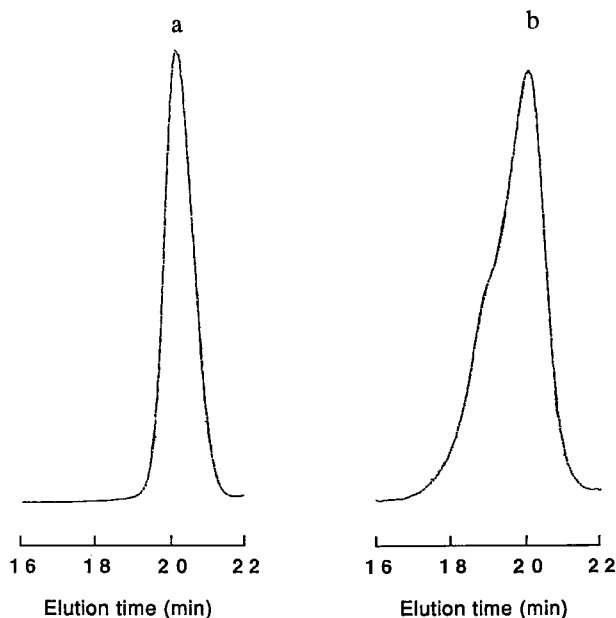


Figure 6 TFMSA-catalyzed reaction of P2c: (a) before reaction; (b) after reaction: P2c 2.22 g (epoxide group 0.2 mmol), TFMSA 15.0 mg (0.1 mmol), toluene 1 mL, 23°C, 30 min.

dimethylsiloxane with a larger chain proceeded, though at a smaller rate. Although phase separation occurred when each P2 was mixed with P1 because of their poor miscibility, in the case of P2a a homogeneous solution was obtained on dilution with toluene under the reaction condition. However, in the case of P2c, the dilution did not make the mixture homogeneous; instead, liquid P2c separated from the toluene solution of P1. The heterogeneous reaction solution containing P2c became homogeneous as the grafting proceeded. This is because the P3 that has been grafted with P2c is miscible, to a certain conversion, with the polydimethylsiloxane. When methanesulfonic acid was used as the catalyst for the grafting of P2c, the reaction solution remained turbid, or heterogeneous, even after prolonged reaction time (24 h), because this acid is less effective than TFMSA for the grafting of a P2 with larger molecular weight, as described above.

A homogeneous solution obtained from the grafting of P2c onto P1 in the presence of TFMSA gradually became turbid when left at room temperature for a long time (more than a week), and then the solution separated into two layers. The phase separation was faster for reaction solutions that contained larger amounts of the acid. The IR spectrum of the upper layer was very similar to

that of P2. It has been reported that 1,4-dioxane is formed in the side reaction of the acid-catalyzed ring-opening polymerization of ethylene oxide.⁵ This result reported in the literature therefore suggests that the reactions shown in Scheme 3 occurred: The TFMSA-catalyzed formation of P3 seems to proceed relatively fast compared with the side reactions—the ring-opening polymerization and dimerization of P2—so that the reaction mixture turns homogeneous first. However, the remaining acid catalyzes the reverse reaction, converting P3 back to P2, and also catalyzes the slow side reactions. Consequently, P2 is finally transformed into P2-I and/or P2-II, which separates from P1, resulting in phase separation.

To examine the side reactions, the change in molecular weight of P2c itself in the presence of TFMSA was followed by GPC. The GPC spectra in Figure 6 shows formation of the reaction products with increased molecular weight. The phase separation was inhibited by neutralizing the residual acidic catalyst with a base such as triethylamine when a homogeneous solution of P3 was obtained after a prescribed reaction time. These results support the assumed mechanism shown in Scheme 3.

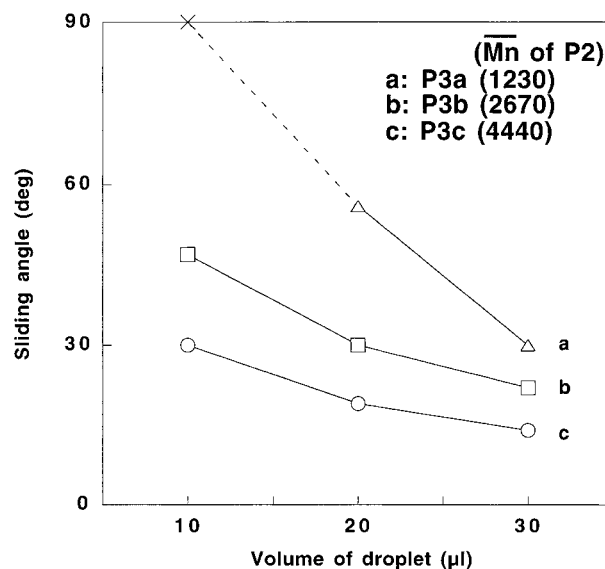


Figure 7 Sliding angles for water droplets on the surfaces of P3 coatings. Synthesis of P3a–c: P1 1.72 g (hydroxyl group 2 mmol), P2a 0.12 g (epoxide group 0.1 mmol) for P3a, P2b 0.27 g (epoxide group 0.1 mmol) for P3b, P2c 0.44 g (epoxide group 0.1 mmol) for P3c, TFMSA 3.0 mg (0.02 mmol), toluene 3.5 mL, 40°C, 1 h. Preparation of coatings: crosslinking agent 0.39 g (isocyanate group 2 mmol), 140°C, 30 min.

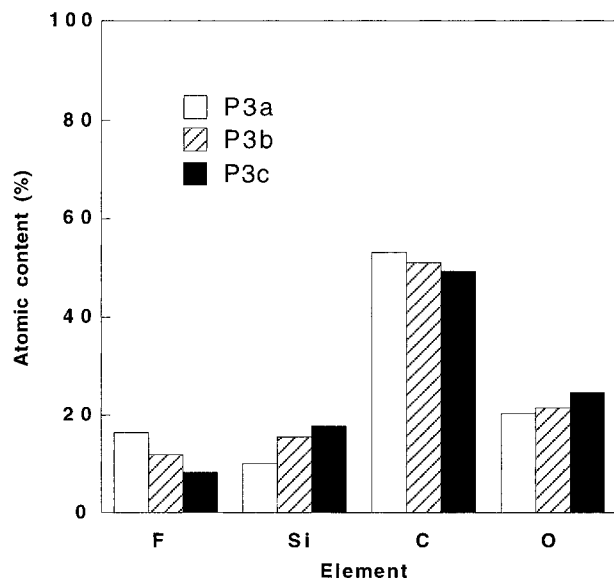
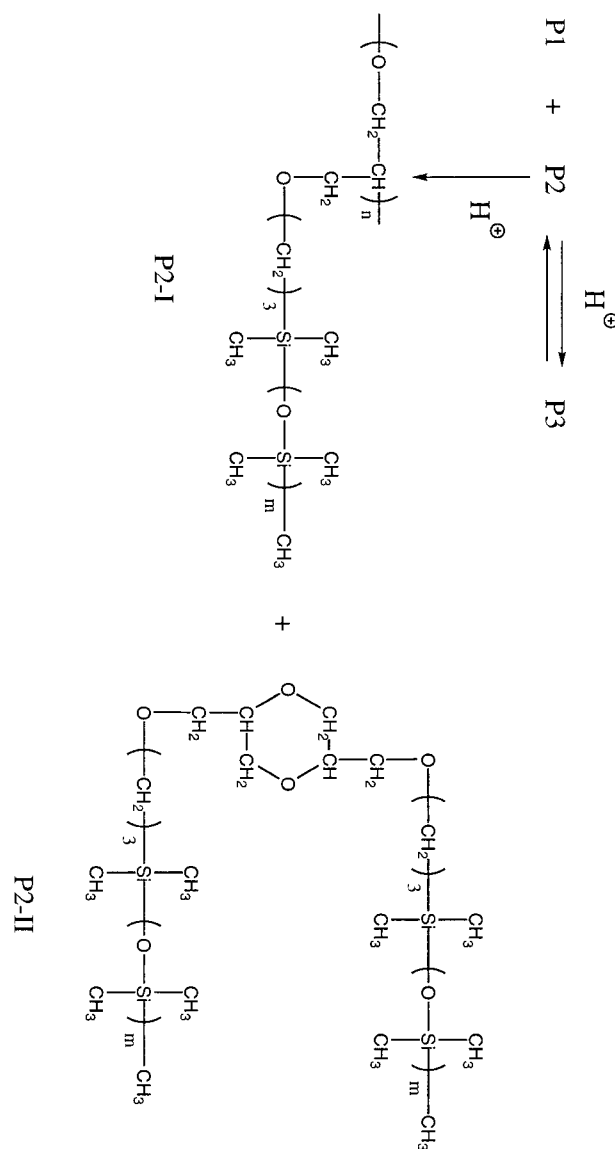


Figure 8 Elemental analysis of the surfaces of P3 coatings by ESCA (the P3 coatings are shown in Figure 7). The atomic contents were calculated on the basis of counted numbers of the elements: $F\% + Si\% + C\% + O\% = 100$.

Sliding of Water Drops

The sliding of water droplets on the surfaces of coatings prepared from polydimethylsiloxane-grafted fluoropolymer (P3) was examined to investigate its hydrophobic, or water-repellent, properties. The data of the grafting reaction indicate that the solutions of P3 for preparation of water-repellent coatings contain certain amounts of unreacted P2. Because free polydimethylsiloxane on the coating surface acts as a lubricant for a water drop,⁶ it was necessary to rule out such effects by removing it from the surface by washing with acetone. As a result, only trace amounts of free P2 were detected in the solvent used for washing the coatings; it seems, therefore, that almost-completed grafting or residual epoxide groups of P2 reacted with isocyanate groups of the crosslinking agent at the temperature of coating formation (140°C), resulting in incorporation of all P2 molecules into the coating network.⁷ Contact angles of water on the coatings were 90.3, 93.0, 96.1, and 96.7° for P1, P3a, P3b, and P3c, respectively. The results of sliding experiments for water droplets on surfaces of the P3 coatings are shown in Figure 7. A water droplet of 10 μL did not slide, even remaining on the vertical plane surface of a coating prepared from P3a, which has the shortest polydimethylsiloxane chains, as well

as on the surface of a coating of ungrafted P1. However, a water droplet of the volume slid on the surface of a coating prepared from P3b, which has longer side chains than P2b, when the tilting angle was 47°. In the case of a P3c coating, the sliding angle for a water droplet of 10 μL was 30°, as seen in Figure 7. These results suggest that longer polydimethylsiloxane side chains are required for P3 with improved hydrophobic properties in order to reduce the sliding angle for water drops. The sliding angles measured on P3c coatings before washing with acetone were almost the same as the values seen in Figure 7. From this it can be inferred that the coatings contain little free polydimethylsiloxane when formed.



Scheme 3

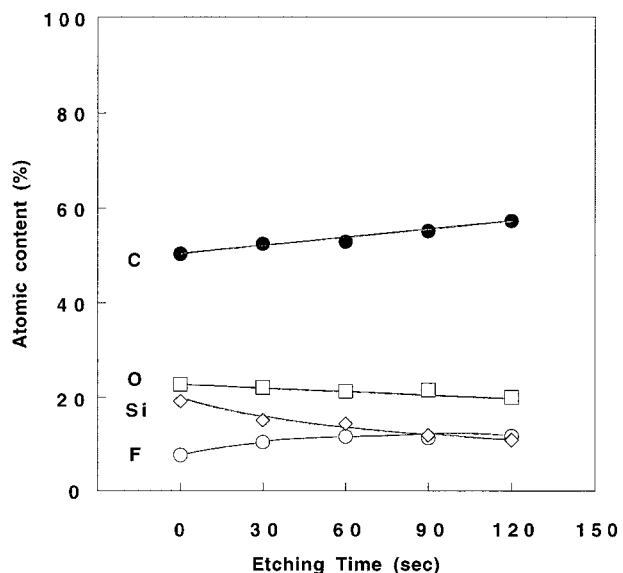


Figure 9 Changes in the atomic contents of the surface of a P3c coating on plasma etching (the P3c coating is shown in Figure 8).

Elemental analysis of the coating surfaces was performed by ESCA (Fig. 8). The surfaces were markedly rich in silicone: the atomic ratio of silicon to fluorine was 2.8:1 on a surface of P3c coating, while the ratio for this polymer is 0.3:1. The difference between the ratios is greater in the case of a coating prepared from a P3 that has longer P2 chains. This finding reveals that polydimethylsiloxane chains moved to the surface during formation of the coatings because their surface energy is smaller than that of the fluoropolymer moiety. The analytical values of the coating surfaces after washing with acetone were unchanged, also indicating the absence of free P2. The elemental content of silicon was the largest on the surface of a P3c coating, on which the smallest sliding angle was observed. P3c bears the longest P2c chains composed of the largest number of dimethylsiloxane units, and the longest chain seems easy to move to the surface of the coating; thus, the silicon content is the largest on the surface of P3c coatings. To examine whether the sliding angle for water droplets depends on the content of dimethylsiloxane units in the surface area, a P3a grafted with an increased amount of P2a was synthesized. A water droplet of 10 μL did not slide on the vertical surface of a coating prepared from the P3a whose dimethylsiloxane unit content was the same as that of the P3c described above. This suggests that the slid-

ing angle depends mainly on chain length of the polydimethylsiloxane branch of P3: the smallest sliding angle for P3c is a result of the longest P2c side chain.

The changes in atomic contents of the surface of a P3c coating on plasma etching is shown in Figure 9. With increasing etching time silicon decreased, which was accompanied by an increase in fluorine, and the atomic ratio of the two elements reached unity after 90 s. Further etching brought the atomic ratio close to that of P3c.

The detailed mechanism for the sliding of water drops on a polydimethylsiloxane surface is unclear. Murase et al.² have shown computed results of the interaction between water molecules and a solid surface composed of siloxane units and fluorinated alkylene moieties. Kawai⁸ related the defined "fall angle" for a water drop on various inclined substrates to polar and dispersion components of their surface energy. Extrand et al.⁹ discussed the retentive force for a drop of water or ethylene glycol on the tilted plane surfaces of solid polymers and silicon wafers by relating this force to the advancing and receding contact angles of the drop. Carre et al.¹⁰ reported on the theoretical analysis of the motion of a water drop on a plane surface of glass treated with a hydrophobic material. Although the sliding mechanism of a water drop on the surfaces of polymer coatings is quite complex to analyze, the materials for coatings on which small water droplets slide easily are expected to be developed for various practical uses. That investigation is now in progress.

CONCLUSIONS

Hydrophobic polymeric materials for coatings were synthesized by grafting polydimethylsiloxane with an epoxide end group onto a fluoropolymer with fluorinated alkylene segments in the main chain and hydroxyl side chains. To evaluate their hydrophobic properties, the sliding of water droplets on the coating surface prepared from the graft polymer was investigated. A small water droplet (10 μL) slid down on the plane surface of the coating of a polymer grafted with relatively long polydimethylsiloxane. This graft polymer seems useful for the preparation of hydrophobic coatings.

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