

# Glow-Discharge-Induced Graft Polymerization of Acrylic Acid onto Poly[1-(trimethylsilyl)-1-propyne] Film

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## SYNOPSIS

Graft polymerization of acrylic acid onto poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] film was examined. The water contact angle of poly(TMSP) film decreased remarkably from 90 to 15° by plasma treatment, which gradually increased up to 40° after several days. When the film exposed to a glow discharge was heated in an aqueous solution of acrylic acid at 80°C for 24 h, graft polymerization proceeded on the film surface, which was confirmed by ATR-IR and ESCA spectra. Graft polymerization effectively occurred above a threshold temperature (80°C). The water contact angle of the grafted film was about 30°, and did not change with time. In contrast, when a poly(TMSP) film exposed to UV irradiation was heated in an aqueous solution of acrylic acid, graft polymerization took place not only on the film surface but also inside the film.

## INTRODUCTION

The surface properties of polymers are as important as their bulk properties, and modifications of the polymer surface have been extensively studied.<sup>1,2</sup> Among them, graft polymerization is one of the most popular methods. In general, graft polymerization exerts a more pronounced effect in modifying a polymer surface than do other methods such as oxidation. Various methods of initiating graft polymerization have been developed, which include plasma treatment (glow discharge or corona discharge),  $\gamma$ -rays, UV light, and redox initiators. Plasma-induced graft polymerization has an advantage that grafting is restricted to the film surface,<sup>3,4</sup> while photo-induced graft polymerization is featured by convenience.<sup>5</sup>

Thus far, we have achieved the synthesis of high molecular weight polymers from various substituted acetylenes by use of groups 5 and 6 transition-metal catalysts.<sup>6</sup> Among those polymers, poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] is characterized by very high permeability to both gases and dissolved oxygen, which triggered intensive

study.<sup>6-8</sup> The surface of poly(TMSP) film is hydrophobic; if it is made hydrophilic, there is a possibility that the film serves as a hydrophilic gas-permeable membrane and/or a more excellent dissolved-oxygen permeable membrane. Whereas the surface energy of polyacetylene film and the introduction of hydrophilic groups to polyacetylene surface have been reported,<sup>9-11</sup> there has been no such study with substituted polyacetylenes.

This article deals with glow-discharge-induced graft polymerization of acrylic acid onto poly(TMSP) film. The film surface turned hydrophilic by the graft polymerization. Effects of reaction conditions on the graft polymerization were examined, and further photo-induced graft polymerization was studied for comparison.

## EXPERIMENTAL

### Materials

Poly(TMSP) was synthesized with TaCl<sub>5</sub> catalyst according to the literature method<sup>12</sup> (polymerization was carried out in toluene at 80°C for 24 h; [TMSP]<sub>0</sub> = 0.50 M, [TaCl<sub>5</sub>] = 20 mM). The weight-average molecular weight of the produced polymer was over 1 × 10<sup>6</sup> (by GPC). Films were prepared by casting polymers from toluene solution (thickness ~ 50

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$\mu\text{m}$ ). Acrylic acid (Wako Pure Chem. Co., Japan) was used after distillation.

### Glow Discharge and UV Irradiation

Glow discharge treatment was carried out with a plasma generator, Ion Coater Model IB-3 (Eiko Co., Japan). A square poly(TMSP) film of  $9\text{ cm}^2$  was placed in the reaction cell (electrode distance 40 mm), and the pressure in the cell was reduced at  $\sim 0.1$  torr. The film was exposed to a glow discharge at an ion current of 6 mA, and then the film was turned over and the same process was repeated. The time of plasma treatment was 60 sec for each side unless otherwise stated.

A 400-W high-pressure Hg lamp was used for photo irradiation; irradiation was carried out from a 5-cm distance in air at  $30^\circ\text{C}$  for 5 min.

### Graft Polymerization

After plasma treatment or photo irradiation, the film sample was exposed to air for a short period ( $< 5$  min), and placed in an aqueous solution of acrylic acid (conc. 10 vol %). The system was degassed and replaced by nitrogen, which was repeated several times. Then polymerization was performed usually at  $80^\circ\text{C}$  for 24 h. After polymerization, the film was washed with water under stirring at  $70^\circ\text{C}$  for 1 d and at room temperature for 2 d to remove the homopolymer formed during graft polymerization. For comparison, only one side of a film was treated with a glow discharge: graft polymerization was carried out and this film was washed by the above procedure; then no homopolymer was found on the untreated side by the ATR-IR spectrum. This indicates that the washing procedure above is appropriate.

### Measurements

The static contact angle of water was measured at  $20^\circ\text{C}$  by the sessile drop method.

The IR and ATR-IR spectra of films were recorded on a Digilab FTS-15E/D spectrophotometer. ATR-IR spectra were measured on a KRS-5 plate (incident angle  $70^\circ$ ). The extent of graft polymerization was compared by an absorbance ratio of the C=O of acrylic acid ( $1,710\text{ cm}^{-1}$ ) and the C=C of poly(TMSP) ( $1,560\text{ cm}^{-1}$ ).

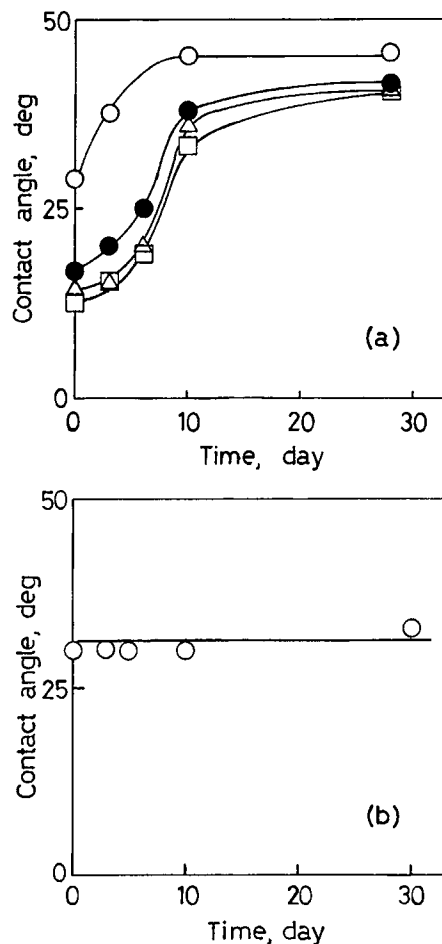
The ESCA measurements were carried out with an ESCA 750 spectrometer (Shimadzu Co., Japan) equipped with a Mg K $\alpha$  X-ray source at a pass energy of 1253.6 eV.

Gas permeation was observed on a K-315-N gas permeability apparatus (Rikaseiki, Co., Japan) equipped with a MKS Baratron detector. Permeation of oxygen dissolved in water was measured by the method in the literature.<sup>13</sup>

## RESULTS AND DISCUSSION

### Treatment of Poly(TMSP) Film with a Glow Discharge

In general, polymer surfaces undergo oxidation on plasma treatment followed by standing in air. Change of the surface of poly(TMSP) film upon exposure to plasma was studied by means of water contact angle [Fig. 1(a)]. The water contact angle

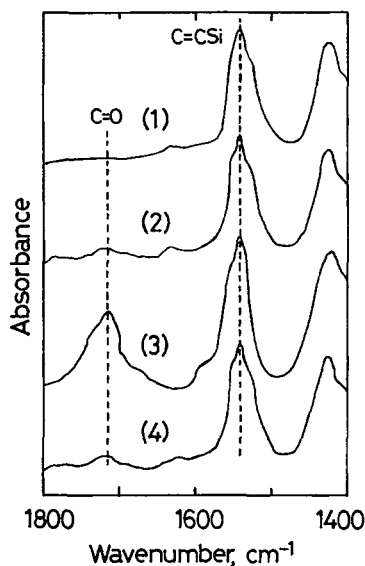


**Figure 1** Change of water contact angle of plasma-treated and graft-polymerized poly(TMSP) film (plasma treated for 60 sec; polymerized in  $\text{H}_2\text{O}$  at  $80^\circ\text{C}$  for 24 h; [acrylic acid] = 10 vol %). (a), plasma-treated; (b), grafted.

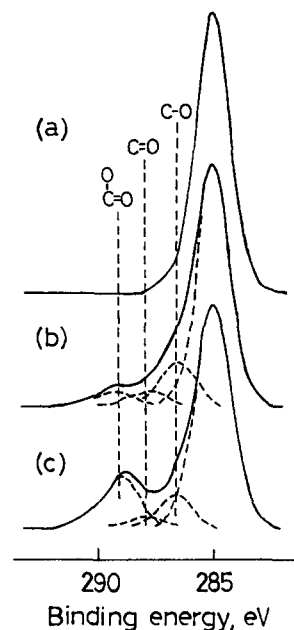
decreased remarkably from  $90^\circ$  (untreated film) to  $15\text{--}30^\circ$  by plasma treatment. This is because radicals were generated on the film surface, and reacted with oxygen in air to form peroxides. Water contact angle decreased progressively (from  $30$  to  $15^\circ$ ) with the increase of treating time (from  $15\text{--}120$  sec). As soon as the film treated with plasma was exposed to air, the water contact angle decreased, indicating quick formation of peroxides. The water contact angle increased when these films were left in air, and leveled off at about  $40^\circ$  after 10 d. It is presumed that peroxides produced on the film surface change into more stable carbonyl and hydroxyl groups gradually. These polar groups are thought to partly shift inside the film; this should be the main reason for the increase of water contact angle with time. On the other hand, as will be described below, the contact angle of the graft polymerized film did not change with time [Fig. 1(b)].

### Glow-Discharge-Induced Graft Polymerization

Graft polymerization on the poly(TMSP) film surface treated by plasma was performed in an aqueous solution of acrylic acid at  $80^\circ\text{C}$  for 24 h. The homopolymer of acrylic acid was produced simultaneously to increase viscosity of the system consid-



**Figure 2** ATR-IR and IR spectra of poly(TMSP) films before and after graft polymerization of acrylic acid (plasma treated for 60 sec; polymerized in  $\text{H}_2\text{O}$  at  $80^\circ\text{C}$  for 24 h; [acrylic acid] = 10 vol %). (a), untreated, ATR; (b), plasma-treated, ATR; (c), grafted, ATR; (d), grafted, IR.



**Figure 3**  $\text{C}_{1s}$  ESCA spectra of poly(TMSP) films before and after graft polymerization (plasma treated for 60 sec; polymerized in  $\text{H}_2\text{O}$  at  $80^\circ\text{C}$  for 24 h; [acrylic acid] = 10 vol %). (a), untreated; (b), plasma-treated; (c), grafted.

erably. Whether graft polymerization occurred or not was examined qualitatively by ATR-IR spectroscopy (Fig. 2). The ATR-IR spectrum of the film treated only by glow discharge [Fig. 2(b)] is similar to that of a pristine film [Fig. 2(a)]. In contrast, the ATR-IR spectrum of the film for which graft polymerization was carried out [Fig. 2(c)] exhibited an absorption due to the carbonyl group of acrylic acid at  $1,710\text{ cm}^{-1}$ . On the other hand, the absorption of the carbonyl group was not observed in the transmission-type IR spectrum of this film [Fig. 2(d)]. Hence, it is concluded that graft polymerization occurred really and only on the film surface.

Figure 3 depicts  $\text{C}_{1s}$  ESCA spectra of untreated, plasma-treated, and graft-polymerized films. The spectrum of a virgin film [Fig. 3(a)] shows only one sharp peak at  $285.0\text{ eV}$ , indicating the absence of the carbon bonded to oxygen. In addition to this peak, three peaks are observed at  $286.5$ ,  $288.0$ , and  $289.0\text{ eV}$  in the film treated by plasma [Fig. 3(b)]. These peaks can be assigned to the carbons of  $\text{C-O}$ ,  $\text{C=O}$ , and  $\text{O-C=O}$ , respectively, on the basis of standard peak positions in the literature.<sup>14</sup> The presence of these peaks confirms the formation of peroxides and the subsequent oxidation to carbonyl and carboxylic compounds. Further, the peaks of  $\text{O-C=O}$  at  $289.0\text{ eV}$  increases in the spectrum of

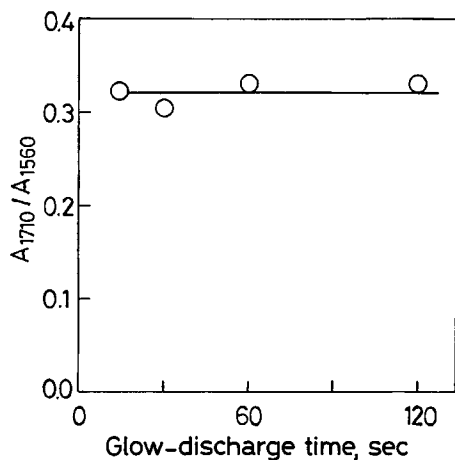
the graft-polymerized film [Fig. 3(c)], which manifests the introduction of acrylic acid by graft polymerization.

The results described above lead to a conclusion that graft polymerization takes place on the film surface when a poly(TMSP) film is exposed to plasma and then heated in an aqueous solution of acrylic acid. On the other hand, graft polymerization did not occur even though a pristine poly(TMSP) film was heated in an aqueous solution of acrylic acid at 80°C; no homopolymer was formed, either. Therefore, it is presumed that thermal cleavage of the peroxides initiates graft polymerization and that the formation of homopolymer during graft polymerization is due to initiation from the hydroxyl radical and/or to chain transfer from graft polymers.

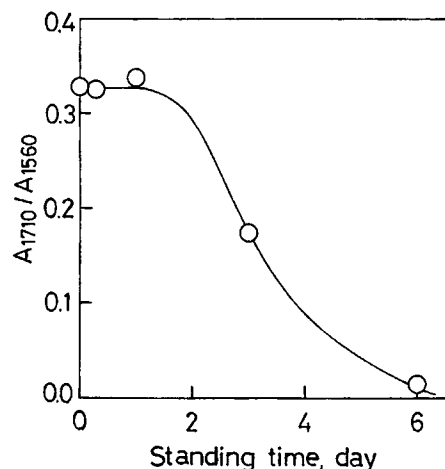
Figure 1(b) shows time dependence of water contact angle of the graft-polymerized film. The contact angle decreased from 90° of the pristine film to 30° by graft polymerization. Even when the graft-polymerized film was allowed to stand in air at room temperature, the contact angle hardly changed with time. This result contrasts to that of the film only treated with plasma. This difference can be interpreted by the concept that it is impossible that a large amount of polar group, which have been introduced onto the surface of the grafted film, shifts inside the film.

#### Effect of Reaction Conditions on the Graft Polymerization

The glow-discharge-induced graft polymerization of acrylic acid was examined under various conditions.



**Figure 4** Effect of plasma-treating time on graft amount (polymerized in H<sub>2</sub>O at 80°C for 24 h; [acrylic acid] = 10 vol %).

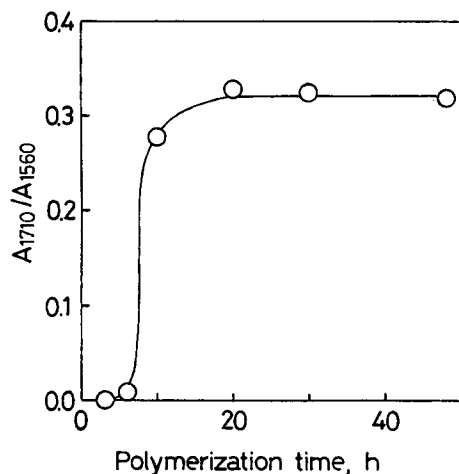


**Figure 5** Effect of the standing time after plasma treatment on graft amount (plasma treated for 60 sec; polymerized in H<sub>2</sub>O at 80°C for 24 h; [acrylic acid] = 10 vol %).

The extent of graft polymerization is discussed on the basis of the absorbance ratio of the C=O of acrylic acid (1,710 cm<sup>-1</sup>) and the C=C of poly(TMSP). The extent of graft polymerization will be tentatively referred to as graft amount below.

Figure 4 shows the dependence of graft polymerization on plasma-treating time. The graft amount hardly changed with the treating time ranging from 15–120 sec. The film treated by plasma was left for various periods of time in air at room temperature, and then graft polymerization was carried out. As seen in Figure 5, the graft amount scarcely changed even though the film was allowed to stand within 1 d before graft polymerization. When the film was left for 3 d, the graft amount considerably decreased. Further, graft polymerization hardly occurred in the case where the film was left for 6 d. These results lead to a conclusion that the lifetime of peroxides that can initiate graft polymerization is several days. The peroxides should gradually change into carbonyl and hydroxyl groups that cannot initiate graft polymerization.

Graft polymerization hardly occurred within a polymerization time of 6 h, which is probably due to the presence of a small amount of oxygen in the system. Graft polymerization proceeded very quickly after about 10 h, and the graft amount hardly changed even after 20 h (Fig. 6). Whereas the viscosity of the system remained low within 8 h, it sharply increased after ≥10 h owing to the formation of homopolymer. Thus, the graft polymerization and the homopolymerization proceed approximately simultaneously.

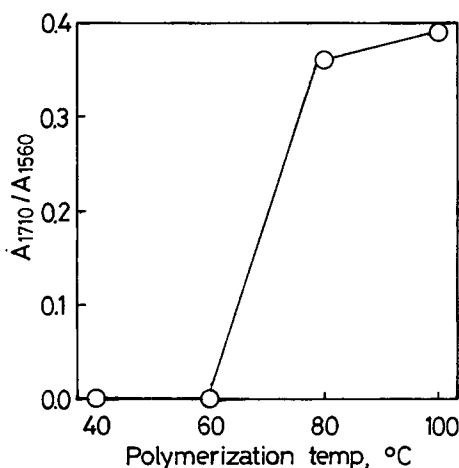


**Figure 6** Effect of polymerization time on graft amount (plasma treated for 60 sec; polymerized in H<sub>2</sub>O at 80°C; [acrylic acid] = 10 vol %).

Figure 7 illustrates the effect of temperature on the graft polymerization. Whereas no graft polymerization occurred below 60°C, it proceeded clearly at 80 and 100°C. This indicates that peroxides that can effect graft polymerization cleave quickly at 80°C and above. A relatively large activation energy for cleavage of the peroxides should be responsible for this temperature dependence.

#### Photo-Induced Graft Polymerization

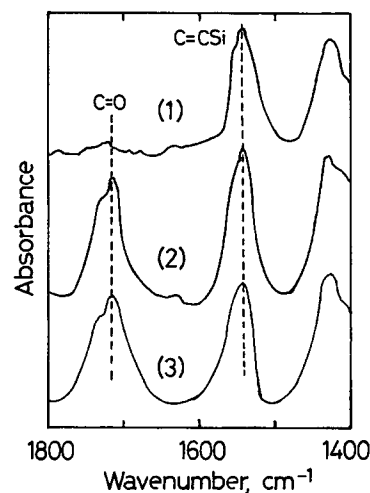
For the sake of comparison with the results of plasma-induced graft polymerization, photo-induced graft polymerization was also studied. Peroxides



**Figure 7** Effect of temperature on graft amount (plasma treated for 60 sec; polymerized in H<sub>2</sub>O for 24 h; [acrylic acid] = 10 vol %).

were generated on a poly(TMSP) film by UV irradiation, and thereafter graft polymerization of acrylic acid was attempted similarly. Poly(TMSP) has an absorption below 290 nm, which overlaps with the light of the high-pressure Hg lamp.

When a poly(TMSP) film was irradiated by UV light in air for 5 min, the water contact angle of the film was similar to that of the untreated one. This implies that the amount of peroxides formed on the film surface is not so large as that for plasma treatment. Then this film was immersed in an aqueous solution of acrylic acid, and heated at 80°C. In the ATR-IR spectrum of the film for which graft polymerization was carried out [Fig. 8(b)], the absorption due to carbonyl group of acrylic acid appeared at 1,710 cm<sup>-1</sup>, indicating that graft polymerization occurred. The absorption was even larger than that for the plasma-induced graft polymerization described above. The transmission-type IR spectrum of the same film [Fig. 8(c)] also shows an absorption due to the carbonyl group, which is as large as the one observed in the ATR-IR spectrum. These spectra imply that the photo-induced graft polymerization took place not only on the film surface but also inside the film. This gives a contrast to the case of plasma-induced graft polymerization in which acrylic acid was grafted only on the surface. It is inferred that, when UV light is used, peroxides are produced inside the film as well, followed by penetration of the monomer into the poly(TMSP) film and grafting. On the other hand, the formation of



**Figure 8** ATR-IR and IR spectra of poly(TMSP) films before and after photo-induced graft polymerization (photo-irradiated for 5 min; polymerized in H<sub>2</sub>O at 80°C for 24 h; [acrylic acid] = 10 vol %). (a), untreated, ATR; (b), grafted, ATR; (c), grafted, IR.

radicals by plasma should be limited to the film surface because plasma cannot easily penetrate into the film.

### Gas and Dissolved Oxygen Permeability

Poly(TMSP) is known to show very high permeabilities to both gases<sup>6</sup> and dissolved oxygen.<sup>13</sup> If these permeabilities are maintained or increased after plasma treatment or graft polymerization, the film will serve as a hydrophilic gas-permeable membrane and/or a more excellent dissolved-oxygen permeable membrane.

The oxygen permeability coefficients of plasma-treated and graft-polymerized poly(TMSP) films were similar to that of the untreated poly(TMSP) film. Thus, hydrophilic poly(TMSP) films with high gas permeability have been obtained in the present study.

Permeability of the oxygen dissolved in water was examined. The permeability coefficient of poly(TMSP) film hardly changed by plasma treatment or graft polymerization of acrylic acid. It is inferred that the introduction of hydrophilic groups reduces boundary-layer resistance but increases through-membrane resistance at the same time, resulting in the negligible change of dissolved-oxygen permeability.

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