

## Electrochemical Polymerization of 6-(*N*-Allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol Monosodium on Aluminum

Fang WANG,<sup>†</sup> Kunio MORI, and Yoshiyuki OISHI

*Chemical Engineering, Faculty of Engineering, Iwate University, Ueda, Morioka 020-8551, Japan*

(Received February 8, 2005; Accepted January 20, 2006; Published May 15, 2006)

**ABSTRACT:** Polymer thin films are prepared by electrochemical polymerization of 6-(*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium on an aluminum plate. The steric and chemical structures of films are characterized by optical ellipsometry, contact angle goniometry, Fourier transform infrared spectroscopy (FT-IR) and impedance spectroscopy. Polymer film thickness and potential applied to the films during electrochemical polymerization, a measure of packing density, increase proportionally to the square root of electrochemical polymerization time following a parabolic law. From FT-IR spectra of the polymer films formed on aluminum plates, only the C–F stretching vibration peak of CF<sub>3</sub>- groups at 1345 cm<sup>-1</sup> is observed, indicating extremely oriented polymer thin film. C1s, N1s and S2p peaks in the XPS spectra indicate that the chemical structure of polymer thin film is poly(6-(*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-disulfide) (PATP) and allyl, tetrahydroperfluorodecyl amino chain axes are perpendicular to the surface, but the triazine ring is aligned parallel to the surface. The contact angle of polymer thin films was 123°, on which a top layer thought to be composed of CF<sub>3</sub>- groups exists. Polymer films on aluminum plates were used to produce parallel plate capacitors having capacitances of 1.33 to 2.06 μF/cm<sup>2</sup>. The dielectric constants of polymer films were calculated to range from 142 to 175, the highest reported for organic dielectrics to date. [doi:10.1295/polymj.38.484]

**KEY WORDS** Triazinedithiol / Electrochemical Polymerization / Polymer Films / High Capacitance /

Much attention on polymer thin films on metallic substrates has been focused on potential applications such as microphotograph,<sup>1</sup> photoresists,<sup>2,3</sup> semiconductors,<sup>4</sup> electric devices,<sup>5</sup> and optical devices.<sup>6,7</sup> Nano-scale polymer films in polymer/metal assemblies are of special interest as microelectronics including capacitors.<sup>8–14</sup> Polymer thin films are mainly prepared by the Langmuir–Blodgett,<sup>15,16</sup> vacuum vapor deposition<sup>17</sup> and self-assembly<sup>18</sup> techniques. Langmuir–Blodgett and self-assembly techniques are very effective when highly ordered arranged monolayers are required, but functionalized compounds and specialized equipment are needed. However, in principle, these two techniques are not suitable on an industrial scale for preparing multilayer polymer thin films on complicated metal surfaces. In vapor-deposition, controlling the orientation and arrangement of films is difficult, but the techniques are suitable for the preparation of multilayer films on metal surfaces.

The polymerization of extremely oriented ordered thin monomer films has been reported.<sup>19,20</sup> Electrochemical polymerization is very effective for preparing multilayer polymer films on complicated metal surfaces without functionalized compounds or specialized equipment. However, little attention has been paid to the formation of ordered and packing polymer

films on metal surfaces by electrochemical polymerization.<sup>21–24</sup>

In this paper, 6-(*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium was polymerized electrochemically on aluminum plates and the chemical structures of polymer thin films were investigated. Parallel plate capacitors having high capacitance were made.

### EXPERIMENTAL

#### *Materials and Reagents*

Aluminum plates (0.1 × 30 × 60 mm) as a working electrode were purchased from the Nilaco Corporation Company. Aluminum test samples for electrochemical polymerization were prepared by cutting these larger plates into pieces 0.1 × 25 × 45 mm in size. 6-(*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium (ATP) was prepared by reacting 6-(*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)amine-1,3,5-triazine-2,4-dichloride with NaSH.<sup>22</sup> Sodium nitrite (NaNO<sub>2</sub>) was used as a supporting electrolyte.

#### *Electrochemical Polymerization*

Electrochemical polymerization of ATP was per-

<sup>†</sup>To whom correspondence should be addressed (Tel: +81-19-621-6322, Fax: +81-19-621-6322, E-mail: t5102008@iwate-u.ac.jp).

formed using electrochemical measurement apparatus (Hotoku Denko Co. LTD. HZ-3000).<sup>21-24</sup> The electrolytic cell was equipped with a working electrode (Aluminum or Stainless Steel Plates), counter electrode (Stainless Steel Plates), and reference electrode (Saturated Calomel Electrode, SCE) and filled with an electrolytic solution containing ATP monomer (5 mmol/dm<sup>3</sup>) and NaNO<sub>2</sub> electrolyte (0.15 mol/dm<sup>3</sup>) in distilled water. Electrochemical polymerization of the ATP monomers was performed galvanostatically.

Polymer films on aluminum plate were used to prepare parallel plate capacitors as follows.<sup>12</sup> Polymer film on aluminum plate was covered by a mask (0.1 × 50 × 70 mm) with a 1 cm<sup>2</sup> cutout. Gold film was then coated on the polymer film using an ionic coater (RMC-Eiko Corp.). Terminals (φ0.01 × 30 mm) were connected to the gold films using silver paste to fabricate plate capacitors.

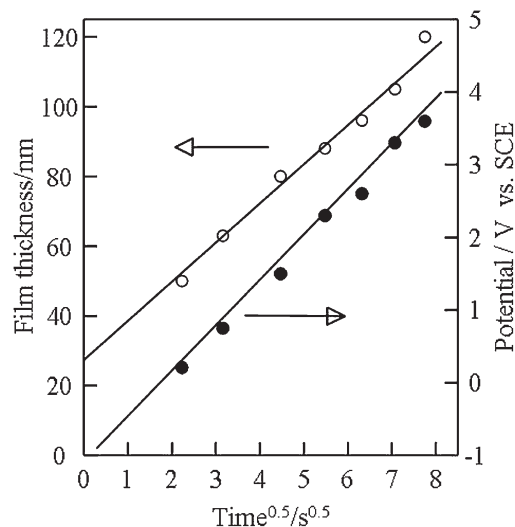
### Measurements

Polymer film thickness was determined using a JASCO M-150i ellipsometer (Jasco Tokyo Japan). FT-IR spectra were measured at a resolution of 4 cm<sup>-1</sup> by high-performance reflection absorption spectroscopy (RAS) using a JASCO IR-5500 (Jasco Tokyo Japan). A reflection attachment was used at an incident angle of 80° together with a wire grid polarizer. Contact angles of pure water on the treated aluminum plates were determined using an Elma goniometer contact angle measuring apparatus (Elma-type G-1). Droplet diameter was controlled at 0.8 to 0.1 mm. X-Ray photoelectron spectroscopy (XPS) was performed to determine the elemental composition of the aluminum surface. Spectra were obtained using a ULVAC PHI-5600 spectrometer with monochrome Al K $\alpha$  radiation (1486.6 eV). Samples were examined over an 800  $\mu$ m area at an incident angle of 45°. Capacitance (Cs), dielectric loss (tan  $\delta$ ), phase angle ( $\theta$ ) and relative dielectric constant ( $\epsilon_r$ ) were obtained at an applied voltage of 0.5 V AC and frequency of 1 kHz. The stabilized electricity source was equipped with capacitors, as recommended by the relevant standard. The relative dielectric constant was calculated from measured capacitance and specimen dimensions.

## RESULTS AND DISCUSSION

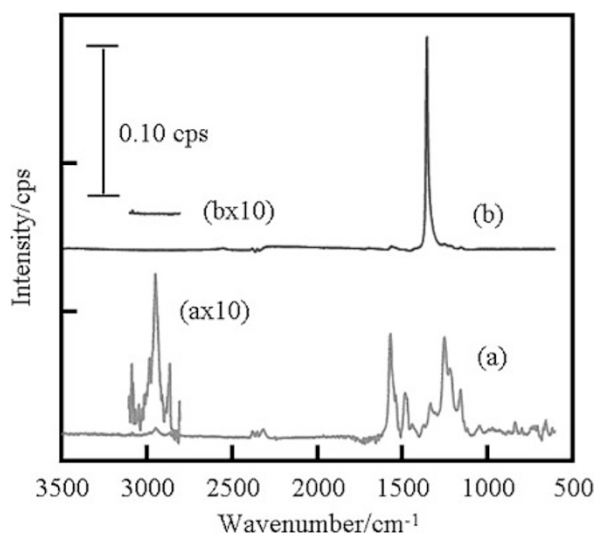
### Polymerization

Electrochemical polymerization of ATP on aluminum plates in 0.15 mol/dm<sup>3</sup> NaNO<sub>2</sub> aqueous solution is shown in Figure 1. The thickness of polymer film on aluminum increased with electrochemical polymerization time in proportion to the square root of time following the parabolic law. Thus, during the film formation process, the diffusion of ATP mole-



**Figure 1.** Effects of square root of polymerization time on the film thickness and potential applied on the polymer film in the electrochemical polymerization of ATP (5 mmol/dm<sup>3</sup>) in 0.15 mol/dm<sup>3</sup> NaNO<sub>2</sub> aqueous solution at 5 °C. Current density: 0.2 mA/cm<sup>2</sup>.

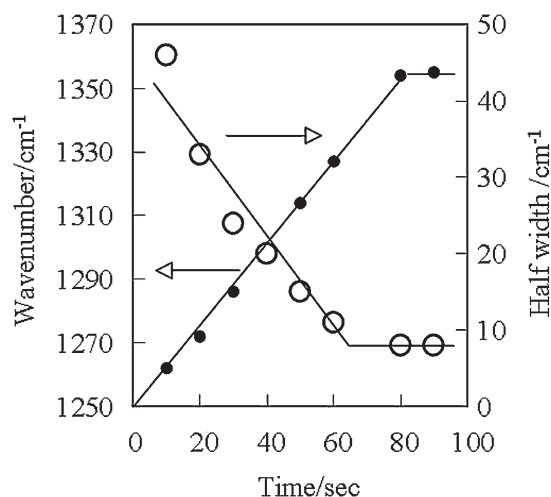
cules determines the rate of formation in the same manner as that in the electrochemical polymerization of 6-dioctylamino-1,3,5-triazine-2,4-dithiol monosodium.<sup>21</sup> Diffusion in ATP has great effect on the formation of polymer films, suggesting that an important factor in electrochemical polymerization is the arrangement of ATP on the metal surface. The polymer films formed are thought to be anisotropic. The potential applied to films formed by electrochemical polymerization of triazine dithiols on metal plates is generally constant under galvanostatic electrolysis.<sup>21-24</sup> However, the potential applied to films formed by electrochemical polymerization of ATP on aluminum plates increased in proportion to the square root of polymerization time. The increase in potential is thought to be a reflection of the thickness and packing density of polymer film, with the potential being a measure of packing density. That is, as polymerization time increases, thickness and packing density of polymer films also increase. Increase in potential in proportion to the square root of polymerization time suggests that the small space between polymer layers decreases with the square root of polymerization time. That is, potential per film thickness increases with polymerization time. For polymerization time of 5 s, potential per film thickness was 10 mV/nm vs. SCE. For 30 s polymerization time, this became 19 mV/nm vs. SCE, and after 60 s of plating increased to 25 mV/nm vs. SCE. The increase in potential per film thickness with polymerization time is mainly due to the packing density of polymer films formed because potential does not generally increase with film thickness on any metal.<sup>21</sup>



**Figure 2.** FT-IR spectra of polymer films obtained by electrochemical polymerization of ATP ( $5 \text{ mmol/dm}^3$ ) on stainless (a) and aluminum (b) plates in  $0.15 \text{ mol/dm}^3$   $\text{NaNO}_2$  aqueous solution for 5 min at  $5^\circ\text{C}$ .

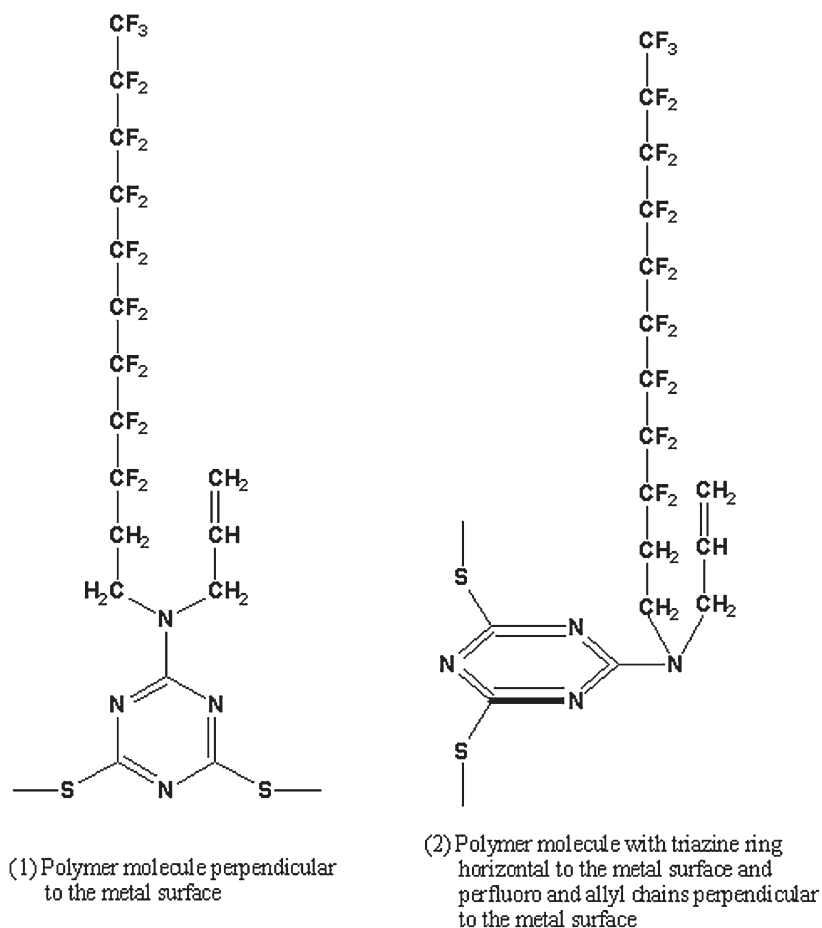
#### Chemical and Polymer Layer Structures

To obtain information about the chemical structure of the polymer film, FT-IR spectra measurements were performed by RAS. Figure 2 shows FT-IR spectra of polymer thin films obtained by electrochemical polymerization of ATP on stainless steel and aluminum plates. In the FT-IR spectrum (a) of stainless steel plate coated by polymer film, the presence of triazine rings was confirmed from absorption peaks at  $1481$ ,  $1536$  and  $1566 \text{ cm}^{-1}$ , due to  $>\text{C}=\text{N}-$  bonds. Allyl perfluorodecyl amino groups were confirmed present from absorption peaks due to C-F stretching vibrations of  $\text{CF}_3$ -groups at  $1250$  and  $1331 \text{ cm}^{-1}$  and  $>\text{CF}_2$ - groups at  $1155$  and  $1219 \text{ cm}^{-1}$ . Peaks ( $a \times 10$ ) of methylene ( $-\text{CH}_2-$ ) and methine ( $>\text{CH}-$ ) groups in polymer films appeared at  $2860$  and  $2917 \text{ cm}^{-1}$ . FT-IR spectrum data revealed that polymer film on stainless steel plate is composed of poly(6-(*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiolane) (PATP). The triazine rings and perfluorodecyl chains in the polymer films on stainless steel plate are oriented perpendicular to the surface, suggesting anisotropic polymer films. However, FT-IR spectra of the polymer films on aluminum plate differed completely from the stainless steel plate samples. On an aluminum plate, only a single peak (b) was observed at  $1331 \text{ cm}^{-1}$  for polymer film obtained by electrochemical polymerization for 20 s, although very slight triazine ring peaks were observed in the wavenumber region of  $1500$  to  $1580 \text{ cm}^{-1}$ . In the region between  $2800$  and  $3000 \text{ cm}^{-1}$ , no peaks were observed, even when magnified 10 times. The peak at  $1331 \text{ cm}^{-1}$  is attributed to C-F bonds in the  $\text{CF}_3$ - of 6-position substituent (perfluorodecyl amino groups). A very low



**Figure 3.** Relation between polymerization time and wavenumber or half width at a peak based on C-F stretching vibration in the polymer film of ATP ( $5 \text{ mmol/dm}^3$ ) in  $0.15 \text{ mol/dm}^3$   $\text{NaNO}_2$  aqueous solution at  $5^\circ\text{C}$ . Current density:  $0.2 \text{ mA/cm}^2$ .

density of triazine rings by RAS indicates that triazine rings in the polymer films are parallel to the aluminum surface. Similarly, methylene and methine groups are barely observed by RAS, indicating that C-H bonds in the polymer films are parallel to the surface. These peaks appear even if perfluorodecyl chains are present either parallel or perpendicular to the surface. Thus, to determine orientation and packing information about allyl perfluorodecyl amino groups in the polymer films, the dependence of position and width of the peak at  $1331 \text{ cm}^{-1}$  on polymerization time were investigated. As shown in Figure 3, the peak shifts to higher wavenumbers in the range of  $1250$  to  $1354 \text{ cm}^{-1}$  with polymerization time and becomes constant at  $1354 \text{ cm}^{-1}$  for polymerization times of over 80 s. The peak that shifts across the range of  $1250$  to  $1354 \text{ cm}^{-1}$  is assigned to C-F stretching vibrations in  $\text{CF}_3$ -groups, as discussed earlier. FT-IR results indicate that the C-F bond is perpendicular to the aluminum surface, with the shift indicating that the C-F stretching vibration in  $\text{CF}_3$ - groups is suppressed in thicker films. Suppression of the C-F stretching vibration is thought due to close packing of perfluoro alkyl chains in the polymer films. Shifts in the C-F stretching vibration stopped for polymerization times of over 80 s, indicating the closest packing to occur at this point. Peaks of C-F stretching vibrations in the  $>\text{CF}_2$ -groups of perfluoro alkyl chains were very small. C-F bonds in this case are thus aligned parallel to the surface. Decrease in half width with polymerization time indicates sharpening of the peak and increased stretching vibration homogeneity, thus suggesting homogeneous formation of closely packed polymer films and layers of  $\text{CF}_3$ - groups in the polymer films are tightly packed. Steric structures of polymer films on



**Figure 4.** Steric structures of polymer films obtained on stainless (1) and aluminum (2) plates.

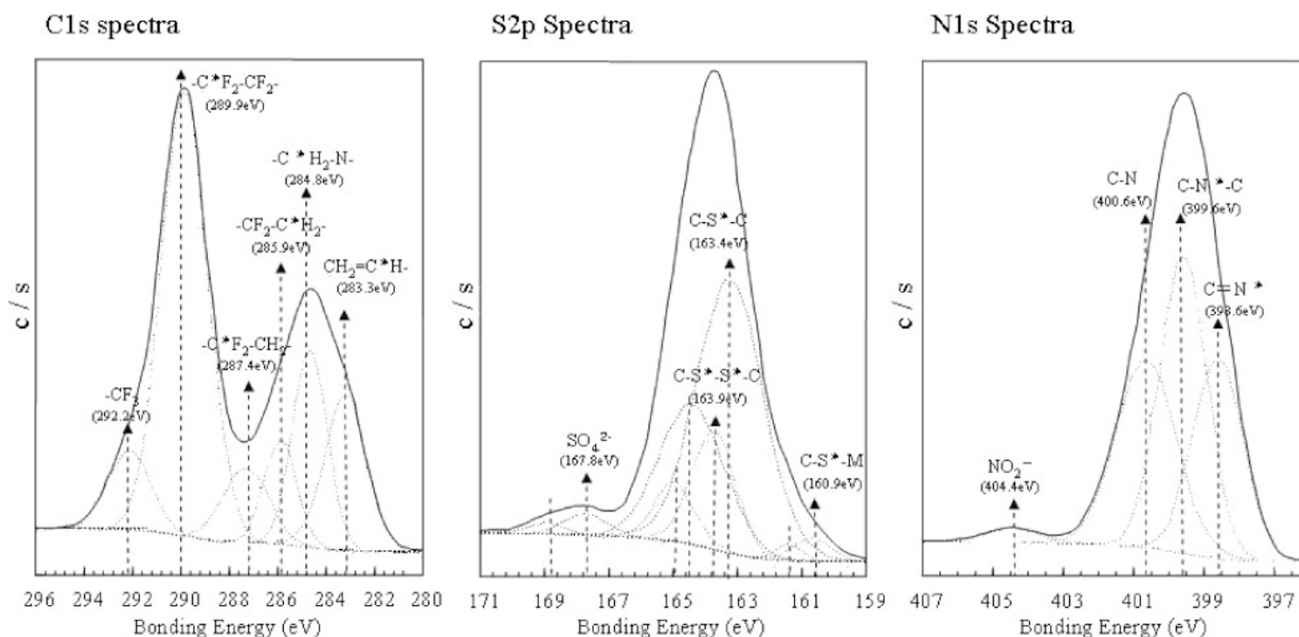
aluminum and stainless steel plates may be concluded to differ, as shown in Figure 4. In PATP polymer films on aluminum plate, triazine rings are parallel to the surface, but in PATP polymer films on stainless steel plate, triazine rings are perpendicular to the surface. Perfluoro alkyl chains in the polymer films on aluminum plate are perpendicular to the surface, but those on stainless steel plate are inclined to the surface. PATP polymer films are concluded to be very highly packed and ordered.

Contact angles in the polymer films on aluminum and stainless steel plates were measured to confirm the structures of top layers of the polymer films. Contact angles on aluminum and stainless steel plates differed, but did not change with polymerization time. The top layer thus always has the same chemical structure composed of  $\text{CF}_3$ - groups. The contact angle on the aluminum surface ( $123^\circ$ ) was slightly greater than on the stainless steel surface ( $117^\circ$ ). This is because perfluorodecyl groups in the polymer films on aluminum are packed closely with  $\text{CF}_3$ - groups and are perpendicular to the surface, whereas perfluorodecyl groups on stainless steel are inclined. Polymer films having layer structure similar to Z-type or Y-type LB films can thus be prepared.<sup>21</sup>

To reconfirm the chemical structures of polymer films grown on aluminum plate, XPS spectra were investigated. Figure 5 shows C1s, N1s and S2p peaks in the XPS spectra of polymer films on aluminum plate. The C1s spectrum was composed of peaks assigned to  $\text{CH}_2=\text{C}^*\text{H}$  groups at 283.3 eV,  $\text{C}^*\text{H}_2\text{N}<$  groups at 284.8 eV,  $\text{CF}_2\text{C}^*\text{H}_2$  groups at 285.9 eV,  $\text{C}^*\text{F}_2\text{CH}_2$  groups at 287.4 eV,  $\text{C}^*\text{F}_2\text{CF}_2$  groups at 289.9 eV and  $\text{CF}_3$  groups at 292.2 eV. These groups suggest the presence of (*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino groups in the polymer films on aluminum plate. The N1s spectrum was composed of peaks assigned to  $\text{C}=\text{N}^*$  groups at 398.6 eV,  $\text{C}-\text{N}^*-\text{C}$  groups at 399.6 eV, and  $\text{N}^*-\text{C}=\text{}$  groups at 400.6 eV, thus indicating triazine rings in the polymer films on aluminum plate. The S2p spectrum consisted of peaks assigned to  $\text{S}^*-\text{M}$  (M; aluminum) groups at 160.9 eV,  $\text{C}-\text{S}^*-\text{C}$  groups at 163.4 eV,  $\text{C}-\text{SS}^*-\text{C}$  groups at 163.9 eV and  $\text{SO}_4^{2-}$  groups at 167.8 eV. Peaks based on  $\text{C}-\text{S}^*-\text{C}$  groups indicate the reaction of SH groups with allylic groups in ATP during electrochemical polymerization. Peaks based on  $\text{C}-\text{SS}^*-\text{C}$  groups indicate the electrochemical reaction of thiols in ATP during electrochemical polymerization.

From the above XPS data, the polymer films ob-





**Figure 5.** C1s, S2p and N1s peaks of XPS spectra of organic films formed on the aluminum plate in 45 tilt degree. X-Ray anode: Al monochromated 2 nm filament, aperture:  $800 \times 200 \mu\text{m}$ .

tained on aluminum plate were reconfirmed to consist of poly(6-(*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)-amino-1,3,5-triazine-2,4-disulfide) and the steric structure of PATP on aluminum plate was determined, as shown in Figure 4.

#### Capacitors

Alkyl thiol chains having axes perpendicular to a metal surface have been reported effective as dielectrics in capacitors having capacitance from 2.5 to  $5.4 \mu\text{F}/\text{cm}^2$ , for which the dielectric constant is 2.7.<sup>14,25,26</sup> Capacitors having high capacitance of Cs ( $\mu\text{F}$ ) can be obtained using organic thin films as dielectrics and relative dielectric constant ( $\epsilon_r$ ) can be calculated from eq 1:

$$\epsilon_r = C_s \times d / (S \times \epsilon_0) \quad (1)$$

where  $S$  ( $\text{cm}^2$ ) is the area of capacitor and  $\epsilon_0$  is the dielectric constant of free space. Generally, an extraordinary dielectric constant can't be obtained because of the lack of extraordinary steric and chemical structures on the metal surface, although the dielectric consists of very thin monolayers of thickness 2.9 to 8.6 nm. These characteristics should be commonplace for capacitance.

Polymer films on aluminum plate have special steric and chemical structures leading to new characteristics. Using polymer films on aluminum plate, parallel plate capacitors were produced. The characteristics of capacitors containing films of various thicknesses as the dielectric material are shown in Table I. Capacitance decreased as polymerization time increased be-

**Table I.** Characteristics of capacitors using organic films differing in thickness as dielectric material

Thickness (nm)	Cs ( $\mu\text{F}/\text{cm}^2$ )	Dielectric Constant (—)	$\tan \delta$ (—)	$\theta$ ( $^\circ$ )
75	2.06	175	0.29	-74
85	1.68	160	0.29	-74
95	1.33	142	0.27	-75
Product <sup>a</sup>	2.5	5.6	0.26	-75

<sup>a</sup>Aluminum electrolytic capacitor in the electronic circuit.

cause film thickness increased. Polymer films have sufficient characteristics for use as capacitors, because the phase angle ( $\theta$ ) and dielectric loss ( $\tan \delta$ ) are nearly the same as in aluminum electrolytic capacitors. Dielectric constant  $\epsilon_r$  of the polymer films was calculated from eq 1, to range from 142 to 175. These are the highest dielectric constants reported to date in organic dielectrics. There appear two reasons why the polymer films on aluminum plate have anomalously relative dielectric constant. One is the incorporation of supporting electrolyte ion species in the electropolymerized thin films. Increasing film thickness caused decrease in dielectric constant. This means that a much more electrolyte ion species resides near the surface of the electropolymerized film. The other reason is special steric structure and close packing of polymer film formed by electrochemical polymerization on aluminum plates. In this case, the arrangement of polymer molecular became ordered and density of the diamagnetic dipole<sup>27,28</sup> of triazine dithiols increased in fixed area, so that high relative dielectric constant of polymer film was induced.

## CONCLUSIONS

6-(*N*-Allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium was polymerized electrochemically on aluminum plate. The thickness of polymer film on an aluminum increased in proportion to the square root of polymerization time, following the parabolic law. As polymerization time increased, the thickness and packing density of polymer films increased. Steric and chemical structures of the fabricated polymer thin films were investigated. FT-IR spectra of polymer films on aluminum only exhibited a single peak based on C–F stretching vibrations of CF<sub>3</sub>- groups at 1345 cm<sup>-1</sup>, suggesting extremely oriented polymer thin film. From the C1s, N1s, and S2p peaks in the XPS spectra, the chemical structure of polymer thin film may be expressed as poly(6-(*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-disulfide (PATP), with the allyl and tetrahydroperfluorodecyl amino chain axes perpendicular to the surface, but the triazine ring parallel to the surface. From contact angle measurements (127°), the top layer of the polymer thin films was found to consist of CF<sub>3</sub>- groups. Polymer films on aluminum plates could be used to produce parallel plate capacitors having very high capacitances of 1.33 to 2.06 μF/cm<sup>2</sup> and the highest dielectric constants (142 to 175) reported to date in organic dielectrics.

*Acknowledgment.* The authors express sincere gratitude for the support of the Japan Science and Technology Corporation under the Joint research Project for Regional Intensive in Iwate Prefecture on “Development of practical applications of magnetic field technology for use in the region and in everyday living”.

## REFERENCES

1. A. Barraud, C. Rosilio, and A. R. Teixeira, *Thin Solid Films*, **68**, 91 (1980).
2. H. Ringsdorf, *Angew. Chem., Int. Ed.*, **12**, 764 (1976).
3. A. Barraud, *Thin Solid Films*, **70**, 317 (1982).
4. B. Mann and H. Kuhn, *J. Appl. Phys.*, **42**, 4398 (1971).
5. V. K. Agawal, *Thin Solid Films*, **50**, 3 (1978).
6. C. W. Pitt and L. M. Walpita, *Thin Solid Films*, **68**, 101 (1980).
7. P. S. Vincett and G. G. Roberts, *Thin Solid Films*, **68**, 135 (1980).
8. C. Zhou, C. J. Muller, and M. A. Peed, *Appl. Phys. Lett.*, **67**, 1160 (1995).
9. H. Fan, H. R. Bently, and L. J. Brinker, *J. Non-Cryst. Solids*, **285**, 79 (2001).
10. R. Subramanian and V. Lakshminarayanan, *Electrochem. Acta*, **45**, 450 (2000).
11. Y. Liu, T. Cui, and K. Varahramyan, *Solid-State Electron.*, **47**, 811 (2003).
12. A. K. Srivastava and H. S. Virk, *Radiat. Phys. Chem.*, **59**, 31 (2000).
13. T. Miyashita and A. Aoki, *Prog. Polym. Sci.*, **18**, 263 (1993).
14. M. A. Rampi, O. J. A. Schueller, and G. M. Whitesides, *Appl. Phys. Lett.*, **72**, 1781 (1998).
15. K. B. Blodgett, *J. Am. Chem. Soc.*, **57**, 1007 (1935).
16. K. Fukuda, H. Nakahara, and T. Kato, *J. Colloid Interface Sci.*, **54**, 430 (1976).
17. Y. Sasabe, *Kogyo Zairyo*, **31**, 31 (1983).
18. Y. Ueda and M. Asida, *J. Electron Microsc.*, **29**, 38 (1980).
19. Y. Shibazaki and K. Fukuda, *Kobunshi*, **26**, 702 (1977).
20. K. Fukuda and H. Nakahara, *Kagaku Sousetu*, **40**, 82 (1983).
21. K. Mori, H. Hirahara, and Y. Oishi, *Langmuir*, **11**, 1431 (1995).
22. K. Mori, Y. Sasaki, H. Hirahara, and Y. Oishi, *Nippon Kagaku Kaishi*, **4**, 281 (2000).
23. K. Mori, H. Hirahara, N. Kumagai, and Y. Oishi, *Electrochem. Solid-State Lett.*, **3**, 546 (2000).
24. K. Mori, Y. Sasaki, H. Hirahara, and Y. Oishi, *J. Appl. Polym. Sci.*, **82**, 2300 (2001).
25. M. D. Porter, T. B. Bright, and C. E. D. Chidsey, *J. Am. Chem. Soc.*, **118**, 8925 (1996).
26. A. Demoz and D. J. Harison, *Langmuir*, **9**, 1046 (1993).
27. T. Mori, K. Mori, and T. Mizutani, *Thin Solid Films*, **388**, 300 (1999).
28. T. Mori, K. Mori, and T. Mizutani, *Thin Solid Films*, **366**, 279 (2000).