Polymer Journal, Vol. 29, No. 4, pp 387—390 (1997)

NOTES

Lithographic Characterization of Poly(4-vinylphenyldimethylvinylsilane) Having Narrow Molecular Weight Distribution

Kazunori SE,† Kohzaburoh MATSUMURA,* Takeo KAZAMA,* and Teruo FUJIMOTO*

Department of Materials Science and Engineering, Faculty of Engineering, Fukui University, Bunkyo 3–9–1, Fukui 910, Japan
* *Department of Chemistry, Faculty of Engineering, Nagaoka University of Technology, Kamitomioka 1603–1, Nagaoka, Niigata 940–21, Japan*

(Received October 3, 1996)

KEY WORDS Lithographic Characterization / Poly(4-vinylphenyldimethylvinylsilane) / Narrow Molecular Weight Distribution / Exposure Response Curve / Negative Resist /

Polymers containing a silylvinyl group as a side chain form intermolecular cross-linkages, and thus can be used as negative working resists.[1,2] Polymers as negative resists must have a narrow molecular weight distribution (MWD).[3–5] Hence, a new monomer, 4-vinylphenyldimethylvinylsilane (VS), which can be polymerized *via* anionic living polymerization, was designed.[6] The structural formula of VS is shown in Figure 1. Another feature of this monomer is that it contains a silicon atom on the side chain. Silicon-based resists[7] can be applied to multi-layer resists[8,9] and submicron lithography due to the fabricated substrate surface.[1,2] We prepared poly(4-vinylphenyldimethylvinylsilane),[6] (PVS) which had a narrow MWD by suppressing side reactions in polymerization. The glass transition temperature of PVS is believed to be higher than room temperature, because PVS is a polystyrene derivative. Hence, PVS is easier to handle for lithographic evaluation compared to ordinary polydiene derivatives.[10–12]

Although lithographic evaluation of PVS varies according to the radiation source and device process requirements, the following are ubiquitous[2]: sensitivity, contrast, resolution, and etching resistance. Special care should be taken forward these lithographic characteristics of PVS that contains no highly efficient cross-linking agents such as bisazide derivatives.[2,13,14] This is the first deep ultraviolet light evaluation and electron beam evaluation of the PVS negative resist.

EXPERIMENTAL

Sample

VS monomer was polymerized[6] using cumylcesium[15,16] as the initiator in a 1 : 2 mixture of diethyl ether/4,4-dimethyl-1,3-dioxane as the solvent at $-78°C$ under 10^{-5} torr for 30 min, and subsequent killing of the living ends was carried out as soon as possible.[6] Table I shows the molecular characteristics of the resultant polymer. The PVS film was deposited onto a silicon wafer by spin-coating a xylene (20 wt%) polymer solution at 500 rpm for 30 s. The film was prebaked at 90°C for 30 min. The thickness of the film was approximately 1.0 μm, measured optically by TALYSTEP (Taylor Hobson Ltd.).

Lithographic Characterization

PVS films were exposed to three different beams: ultraviolet (UV) light using a Cannon PLA-500 with wavelength of 405 nm (12.0 mW cm^{-2}), deep UV light using a Cannon PLA-502F equipped with a Cannon CM-290 with wavelength of 290 nm (29 mW cm^{-2}), and an electron beam using a Hitachi HHS-2R (ACC. Voltage = 10 kV, beam current = 2.7×10^{-11} A, spot diameter = 0.25 μm).

The exposed wafers were dip-developed for 30 s at room temperature in several mixed solvents. The wafers were subsequently rinsed in ethanol for 1 min at room temperature and then postbaked at 60°C for 30 min. Film thickness was measured optically by TALYSTEP (Taylor Hobson Ltd.). Contrast tests were carried out using OAI-205 (Optical Associate Inc.). Dry etching durability to reactive ion etching (RIE) was investigated, under O_2 and $O_2/CF_4 = 4/96$, using OAPM-300 (Tokyo

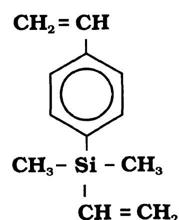

Figure 1. Structural formula of 4-vinyphenyldimethylvinylsilane (VS).

Table I. Molecular characteristics of poly(4-vinylphenyldimethylvinylsilane)

Sample	$10^{-4} M_n$[a]	M_w/M_n[b]
PVS-1	2.0_5	1.0_5
PVS-2	4.5_9	1.0_8
PVS-3	4.8_1	1.0_8
PVS-4	$13._6$	1.0_3

[a] Number average molecular weights determined by membrane osmometry. [b] Molecular heterogeneity determined by GPC measurement using standard polystyrenes.

† To whom all correspondence should be addressed (Tel: +81–776–27–8957, Fax: +81–776–27–8767).

Ohka Ltd.) with an etching energy of 25W, a vacuum of 1.9 Torr, and table temperature of 100°C.

RESULTS AND DISCUSSION

Understanding of the mechanism of radiation cross-linking[13,17] for PVS film was essential for the development of this new negative working resist and this required detailed clarification of the radiation chemistry of PVS. This paper presents the first deep ultraviolet light evaluation and electron beam evaluation for the PVS negative working resist.

Deep UV Light

After exposure for 30 s to an ultraviolet (UV) light having a wavelength of 405 nm, spin-coated film was developed using the method in the Experimental Section. No gel was observed in the exposed area. PVS could not act as a negative resist forward UV light.

To obtain high resist performance for a deep UV light (290 nm), several photolabeling agents[20] and efficient cross-linking agents[13,14,21] are usually added to resist polymers. By these lithographic agents, high absorbance of the resists can be obtained in a deep UV light. Cross-linking for negative resist occurs through various mechanisms. However, a cyclohexane solution of PVS exhibits absorption at 270 nm—300 nm ($\log \varepsilon = 2.2$ at $\lambda = 290$ nm). Therefore, deep UV evaluation of PVS containing no efficient cross-linking agents such as bisazide derivatives[2,13,14] was carried out. Resist films have low absorption characteristics[2] that permit uniform imaging through the thickness of the resist films. The transmittance of PVS film of 1.0 μm thickness was 0.82 at $\lambda =$ 290 nm based on a molar extinction coefficient of $\log \varepsilon =$ 2.2.

Following exposure to deep UV light of intensity from 135 mJ cm^{-2} to 166 mJ cm^{-2}, a spin-coated film was developed. Figure 2 shows line and space test patterns which have 2.0 μm lines and 0.75 μm spaces (abbreviated as 2.0 μm in the figure), 1.5 μm lines and 0.75 μm spaces (1.5 μm), 1.0 μm lines and 0.75 μm spaces (1.0 μm), and 0.50 μm lines and 0.75 μm spaces (0.50 μm). Gels were observed in exposed areas but not in unexposed areas. Therefore, this film appears to act as a negative resist. Following exposure to 135 mJ cm^{-2}, the lowest intensity, a test pattern of 0.50 μm lines and 0.75 μm spaces showed webbing and meandering of the lines. The two other patterns showed clear image lines without webbing or meandering.

Sensitivity of negative resists is defined[1,4] as $D_g^{0.5}$, which represents the intensity of light-forming a normalized half-thickness of a film. Contrast of a negative resist is defined as follows[1,2,5]:

$$\gamma_1 = [\log(D_g^{\exp}/D_g^i)]^{-1} \tag{1}$$

$$\gamma_2 = [2\log(D_g^{0.5}/D_g^i)]^{-1} \tag{2}$$

$$\gamma_3 = [dh/d(\ln Dose)]_{h=0} \tag{3}$$

Where $D_g^{\exp}$ represents the intensity of light-forming gels of thickness similar to initial film thickness, D_g^i represents the intensity of a light-forming gel which forms a gel point, h represents the normalized gel thickness, and *Dose* represents the exposure energy. If an exposure response

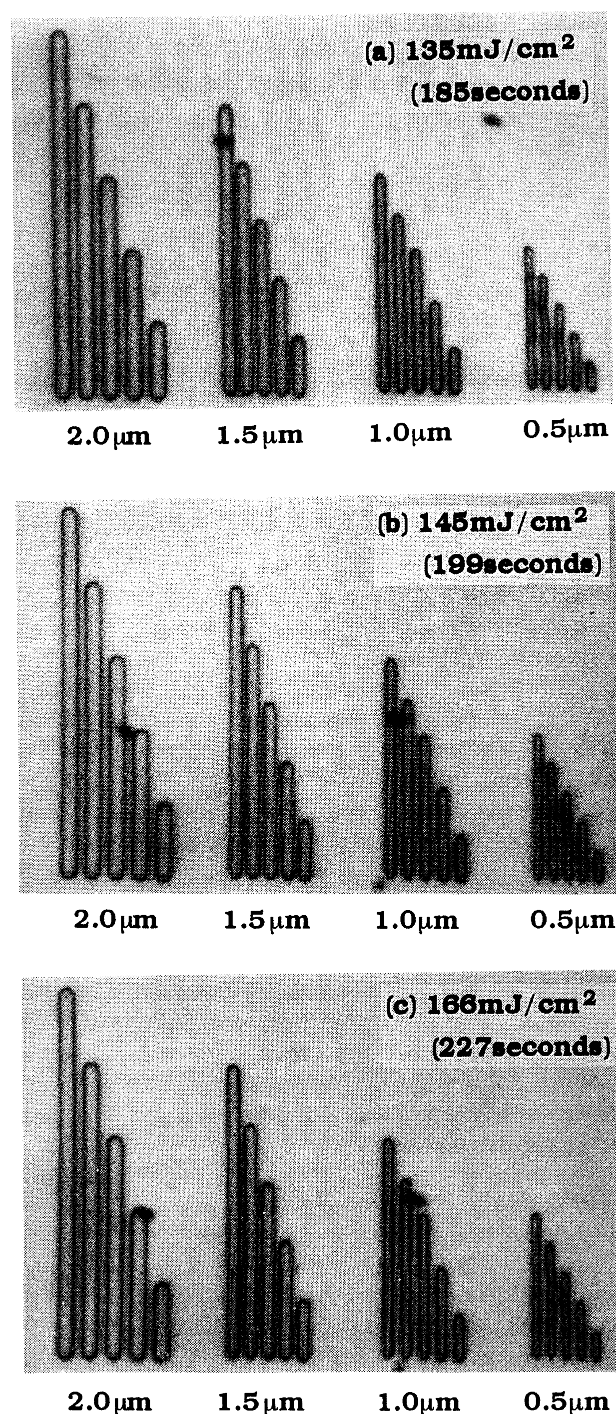

Figure 2. Scanning electron micrograph of image lines from a resist of PVS-4 films exposed to deep UV light of 270 nm. The developer is a mixture of xylene–methanol = 8 : 1. A number such as 2.0 μm appearing in this figure represents 2.0 μm lines, and all spaces between the lines are 0.75 μm. Intensities of a deep UV light are (a) 135 mJ cm^{-2} (185 seconds), (b) 145 mJ cm^{-2} (199 seconds), and (c) 166 mJ cm^{-2} (227 seconds).

curve is symmetrical with respect to a normalized gel thickness of 0.5, the values of γ_1, γ_2, and γ_3 should coincide with each other. The exposure response curve of PVS-4 exposed to deep UV light was found to be qualitatively the same as those of PVS-4 exposed to an electron beam. From the exposure response curve, deep UV evaluation of PVS-4 was made. The resultant lithographic characteristics of PVS-4 are shown in Table II.

Favorable values of lithographic characteristics of

Table II. Lithographic characteristics of PVS thin films spin-coated onto silicon wafers

Sample	$10^{-4} M_n$[a]	Light	Sensitivity[b]	Contrast values[b]		
			$D_g^{0.5}$	γ_1	γ_2	γ_3
PVS-1	2.5_0	UV light[c]				
PVS-4	$13._6$	Deep UV light	$19\,mJ\,cm^{-2}$	1.4	3.8	2.3
PVS-1	2.5_0	Electron beam	$7.0 \times 10^{-6}\,C\,cm^{-2}$	1.3	2.8	2.1
PVS-4	$13._6$	Electron beam	$2.1 \times 10^{-6}\,C\,cm^{-2}$	1.4	3.6	2.3

[a] Number average molecular weights determined by membrane osmometry. [b] Symbol for $D_g^{0.5}$, γ_1, γ_2, and γ_3 are explained in the text. [c] No gel was observed in the exposed area.

common negative resists exposed to deep UV light have been reported as follows[1,2,13,14,22]: $D_g^{0.5}$ (sensitivity) of $30\,mJ\,cm^{-2}$, resolution of 0.4 μm, and γ (contrast) of 3—5. The resultant PVS resist thus appears to possess favorable lithographic characteristics.

Electron Beam

After exposure to an electron-beam, PVS films were developed in a mixture of xylene–methanol = 8 : 1. Figure 3 shows line and space test patterns of 1.0 μm lines and 1.0 μm spaces, 1.5 μm lines and 1.0 μm spaces, 2.0 μm lines and 1.0 μm spaces, and 2.5 μm lines and 1.0 μm spaces. Gels were observed in exposed areas. Webbing and meandering of lines were not observed in these films. Thus, these test patterns show PVS to act as negative resists to an electron beam.

As shown in Figure 4, exposure response curves of PVS-1 differed according to the developer used, but not remarkably. In contrast, exposure response curves of PVS-4 ($M_n = 13._6 \times 10^4$) for all developers are located at lower energy levels than are those of PVS-1 ($M_n = 2.5_0 \times 10^4$). Therefore, lithographic characteristics were determined based on representative exposure response curves of PVS-1 using methyl ethyl ketone and PVS-4 using ethyl acetate–isopropyl acetate = 1 : 1. The results are summarized in Table II.

As with many negative electron resists,[23,24] increase in molecular weight results in increase of sensitivity, but this gradually decreases the resist contrast.[7,25] As expected, the sensitivity of PVS was found to increase with molecular weight; $D_g^{0.5}$ PVS-4 was 30% smaller than that of PVS-1. This is broadly in agreement with Choong and Kahn.[25] Contrast varied widely from γ_1 to γ_3, because exposure response curves were not symmetrical with respect to a normalized gel thickness of 0.5, but saturated with gels above a normalized gel thickness of 0.8. As shown in Table II, the γ_1 and γ_2, respectively, are the smallest and largest of the three contrast values. Thus, γ_3 is believed to be important for contrast properties. The same was observed when the samples were exposed to deep UV light. γ_3 of PVS-1 and PVS-4 were 2.1 and 2.3, respectively. These contrast values are higher than those of common resists prepared radically.[1,2,5] Another important fact is that contrast did not decrease with increasing molecular weight, possibly due to a narrow molecular weight distribution (M_w/M_n less than 1.0_5) of both PVS films anionically prepared.

Favorable lithographic characteristics of common negative resists exposed to an electron beam have been reported as follows[23,24,28,29]: $D_g^{0.5}$ (sensitivity) of $1 \times 10^{-6}\,C\,cm^{-2}$, resolution of 0.3 μm, γ (contrast) of 3—6, and excellent dry etching durability to reactive ion etching. The resultant PVS-4 thus appears to have favorable lithographic characteristics.

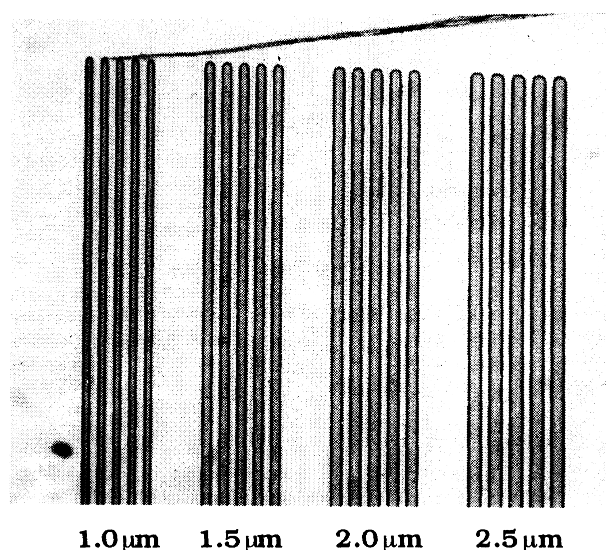

Figure 3. Scanning electron micrographs of image lines from resists of PVS-4 film exposed to an electron beam. A developer is a mixture of xylene–methanol = 8 : 1. A number such as 1.0 μm appearing in this figure represents 1.0 μm lines, and all spaces between the lines are 1.0 μm.

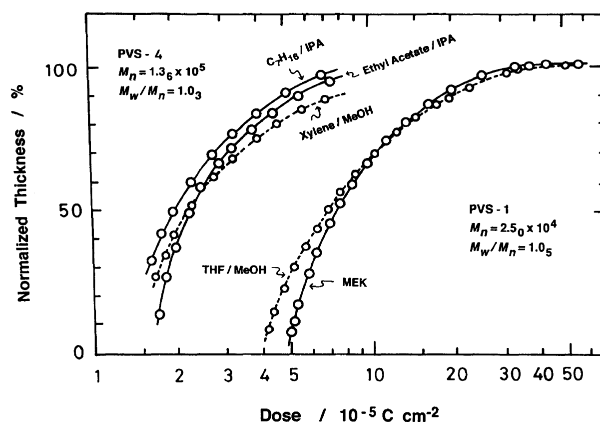

Figure 4. Exposure response curves of PVS-1 and PVS-4 exposed to electron beams. Developers in the figure are *n*-heptane(C_7H_{16})–isopropyl acetate(IPA) = 1 : 1, ethyl acetate–isopropyl acetate(IPA) = 1 : 1, xylene–methanol(MeOH) = 8 : 1, methyl ethyl ketone (MEK), and tetrahydrofuran (THF)–methanol(MeOH) = 35 : 65.

Dry Etching Durability

Two tests of dry etching durability to a reactive ion etching O_2 plasma (abbreviated as O_2 RIE) and reactive

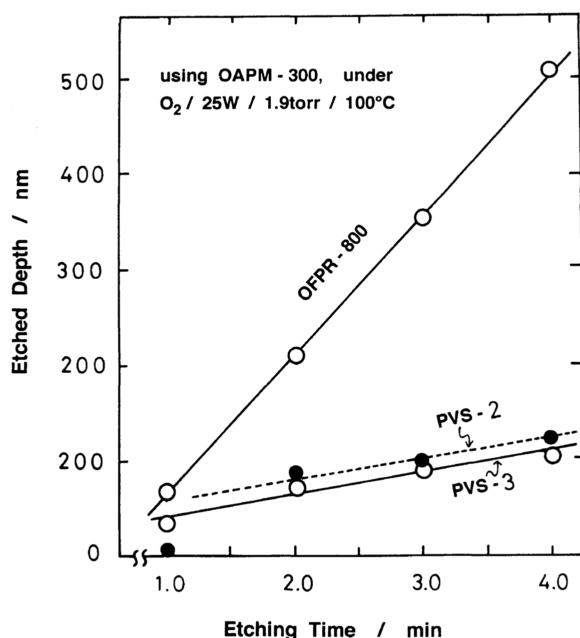

Figure 5. Plots of etching depths of PVS-2 and PVS-3 *vs.* etching time under O_2 reactive ion etching. Etching rate can be determined from the slope. The result for OFPR-800 (a commercial phenol-novolak resist) is also shown for reference.

ion etching $CF_4/O_2 = 96/4$ plasma (abbreviated as CF_4/O_2 RIE) were carried out. A representative positive photo resist, OFPR-800[1,2,28] (commercial phenol-novolak resist, Tokyo Ohka Ltd.), was also tested for reference. In CF_4/O_2 RIE, two PVS films were found to have an etching rate of 77 nm min^{-1}, the same as that of OFPR-800.[18,19] Figure 5 shows the relationship between etching depth and etching time in O_2 RIE. PVS-2 ($M_n = 4.5_9 \times 10^4$, $M_w/M_n = 1.0_8$) and PVS-3 ($M_n = 4.8_1 \times 10^6$, $M_w/M_n = 1.0_8$) were found to have an etching rate of 21 nm min^{-1}. This value is 15 percent that of OFPR-800 (143 nm min^{-1}). AZ-1350 resist (phenolic resin containing azide compound)[1,2] has been reported to be etched at a rate of 80 nm min^{-1}.[7] A precise etching rate comparison for PVS and AZ-1350 was not performed in the present study, because experimental conditions for O_2 RIE are not exactly the same for different substances. However, the etching rate of PVS was found to be 25 percent that of AZ-1350. Thus, PVS shows excellent dry etching durability to O_2 RIE.[29,30]

In conclusion, PVS containing a silylvinyl group as a side chain was found to act as negative working resist by exposing to deep UV light and an electron beam. The lithographic characteristics of PVS having a narrow MWD are reported in this paper for the first time. More systematic experiments and detailed lithographic evaluation of PVS are needed for preparation of a new polymer for use as a negative resist.

Acknowledgments. The authors thank Mr. S. Asaumi, Tokyo Ohka Kogyo Co., Ltd., Kanagawa, Japan, for assistance in carrying out deep UV light evaluation of PVS, and Mr. T. Nakata, Electronic Components Operations, Dai Nippon Printing Co., Ltd., Saitama, Japan, for his assistance with performing electron beam evaluation of PVS.

REFERENCES

1. L. F. Thompson, C. G. Willson, and J. M. Frechet, in "Materials for Microlithography," ACS Symposium Series 266, American Chemical Society, Washington, DC., 1984.
2. L. F. Thompson, C. G. Willson, and S. Tagawa, in "Polymers for Microelectronics, Resists and Dielectrics," ACS Symposium Series 537, American Chemical Society, Washington, DC., 1994.
3. E. D. Feit and L. E. Stillwagon, *Polym. Eng. Sci.*, **20**, 1058 (1980).
4. L. J. Lai and L. T. Shepherd, *J. Electrochem. Soc.*, **126**, 696 (1979).
5. K. Itaya, K. Shibayama, and T. Fujimoto, *J. Electrochem. Soc.*, **129**, 663 (1982).
6. K. Se, K. Matsumura, T. Kazama, and T. Fujimoto, *Polym. J.*, to be submitted.
7. S. Imamura, T. Tanaka, K. Harada, and S. Sugawara, *J. Appl. Polym. Sci.*, **27**, 937 (1982).
8. J. M. Moran and D. J. Maydan, *Vac. Sci. Technol.*, **16**, 1620 (1979).
9. B. Lin, *J. Solid-State Technol.*, **26**, 105 (1983).
10. S. Nonogaki, H. Morishita, and N. Saitou, *Appl. Polym. Symp.*, **23**, 117 (1974).
11. K. Itaya, T. Fujimoto, M. Todoku, M Fukuda, and K. Kihara, *Semiconductor and Integrated Circuit Prepr. Jpn.*, **23**, 24 (1982).
12. M. Endo, Y. Tani, M. Sasago, and N. Nomura, *J. Electrochem. Sci.*, **136**, 2615 (1989).
13. S. X. Cai, J. C. Nabity, M. N. Wybourne, and J. F. W. Keana, *Chem. Mater.*, **2**, 631 (1990).
14. S. X. Cai, J. F. W. Keana, J. C. Nabity, and M. N. Wybourne, *J. Mol. Electron.*, **7**, 63 (1991).
15. K. Se, O. Watanabe, Y. Isono, and T. Fujimoto, *Makromol. Chem., Makromol. Symp.*, **25**, 249 (1989).
16. K. Se, M. Kijima, and T. Fujimoto, *Polym. J.*, **20**, 791 (1988).
17. J. H. O'Donnel, N. P. Rahman, C. A. Smith, and D. J. Winzor, *Macromolecules*, **12**, 113 (1979).
18. R. A. Jones, G. A. Salmon, and I. M. Ward, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **35**, 878 (1994).
19. E. S. Castner and V. Galiatsatos, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **35**, 959 (1994).
20. R. Aggeler, K. Chicas-Cruz, S. X. Cai, J. F. W. Keana, and R. A. Capaldi, *Biochemistry*, **31**, 2956 (1992).
21. T. Iwayanagi, *J. Electrochem. Soc.*, **27**, 2759 (1980).
22. D. Wheeler, C. Boyce, R. Hutton, S. Stein, R. Cirelli, F. Biocchi, M. Cheng, and G. Talor, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **35**, 940 (1994).
23. R. Sezi, R. Leuschner, M. Sebald, H. Ahne, S. Birkle, and H. Borndorfer, *Microelectronic Eng.*, **11**, 535 (1990).
24. A. Tamura and M. Sato, *Proc. SPIE*, **1465**, 35 (1991).
25. H. S. Choong and F. L. Kahn, *J. Vac. Sci. Technol.*, **19**, 1121 (1981).
26. V. T. Stannett, G. L. Grune, and R. T. Chern, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **35**, 876 (1994).
27. N. Kihara, T. Ushirogouchi, T. Tada, T. Naito, S. Saito, and M. Nakase, *J. Electrochem. Soc.*, **141**, 3161 (1994).
28. V. K. Sharma, S. Affrossman, and R. A. Pethrick, *Polymer*, **25**, 1087 (1984).
29. H. Shimada, M. Onodera, S. Shimomura, K. Hirose, and T. Ohmi, *J. Electrochem. Soc.*, **139**, 1721 (1992).
30. T. J. Dalton, W. T. Conner, and H. H. Sawin, *J. Electrochem. Soc.*, **141**, 1893 (1994).