Journal of Photopolymer Science and Technology
Volume16,Number4(2003)601−606©2003TAPJ

A New Photoresist Materials for 157nm Lithography-3: Poly[2-hydroxy-3-pinanyl vinyl sulfonate-*co*-4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene]

H. Iimori[1], S.Ando[1], Y. Shibasaki[1], M.Ueda[*1],
S. Kishimura[2], M.Endo[2], M.Sasago[2]

*[*1]Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama 2-12-1 Meguro-ku, Tokyo 152-8552, Japan*
mueda@polymer.titech.ac.jp *[*2]ULSI Process Technology Development Center, Semiconductor Company, Matsushita Electric Industrial Co., Ltd., 19, Nishikujo-Kasuga-cho, Minami-ku, Kyoto 601-8413, Japan*

A new photoresist for 157 nm lithography on the basis of poly[(2-hydroxy-3-pinanyl vinyl sulfonate)-*co*-4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene] [**poly(VSO$_3$Pina$_{73}$-*co*-HFISt$_{27}$)**] and triphenylsulfonium perfluoro-1-butanesulfonate (**TPS-Nf**) as a photoacid generator (**PAG**) has been developed. Poly(**VSO$_3$Pina**-*co*-**HFISt**)s were prepared by free radical polymerization of **VSO$_3$Pina** with **HFISt**. The photoresist consisting of poly(**VSO$_3$Pina$_{73}$**-*co*-**HFISt$_{27}$**) and 4 wt% **TPS-Nf** showed a sensitivity of 10 mJ cm^{-2} and a contrast of 6, when it was exposed to 157 nm laser and developed with 0.6 wt% aqueous tetramethylammonium hydroxide (**TMAH**) solution at 25 °C. A fine positive image of 140 nm line and space patterns was printed in a film, which was exposed to 15 mJ cm^{-2} by a contact printed mode. The resist film showed an optical density (**OD**) value of 3.6 μm^{-1} at 157 nm wavelength.

Keywords: 157-nm photolithography / poly[(2-hydroxy-3-pinanyl vinyl sulfonate -*co*-4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene) / photoacid generator / chemically amplified photoresist.

1. Introduction

Optical lithography continues to extend its resolution limit and may reach the 65-nm node using a 157-nm technology.[1] A polymer designed for 157-nm lithography has to compromise properties such as high transparency, etch resistance, and a chemically amplified solubility change. In particular, high transparency at 157 nm is the most important factor in the design of photoresist materials because most common lithographic materials, including commercial photoresists, strongly absorb the 157-nm radiation. Since highly fluorinated polymers are sufficiently transparent in this region, poly(methyl α-trifluoromethylacrylate),[2] poly[4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene] [poly(**HFISt**)],[3] poly[5-(2-trifluoromethyl-1,1,1-trifluoro-2-hydroxypropyl)-2-norbornene],[4] and other fluorinated polymers [5] have been reported as single-layer photoresists for 157-nm lithography. On the other hand, dissolution inhibitor for 157nm have been reported.[6]

In previous papers, we reported that time-dependent density functional theory (TD-DFT) calculations using the B3LYP hybrid functional with the 6-311++G(d,p) basis set is a very useful tool to predict the transparency of molecules in the VUV region, and in particular, useful for the design of photoresist materials for F$_2$ lithography.[7] On the basis of this calculation method, copolymers from vinylsulfonyl fluoride or vinyl sulfonates with **HFISt** have been found to be quite transparent at 157 nm, and their *tert*-butoxycarbonyl (t-BOC)-protected copolymers

Received May 6, 2003
Accepted June 5, 2003

functioned as positive alkaline developable 157-nm resists.[8] Recently monosulfonates of 2,3-pinanediol was reported to exhibit excellent storage stability and non-linear acid-proliferation ability, and to markedly enhance photosensitivity of chemically amplified photoresists for 193-nm photolithography.[9] Ichimura et al. reported a novel positive-working photoresist, in which composition of 2-hydroxy-3-pinanyl *p*-styrenesulfonate acted as an acid amplifier.[10] We prepared and evaluated various poly(vinyl sulfonate)s, and found that poly(2-hydroxy-3-pinanyl vinyl sulfonate) (**VSO_3Pina**) was easily hydrolyzed to the poly(vinyl sulfonic acid) in the presence of a catalytic amount of methanesulfonic acid. This finding prompted us to develop a new 157-nm resist on the basis of poly(**VSO_3Pina**).

This article reports a novel 157-nm resist system based on poly[**VSO_3Pina** -*co*-(**HFISt**)] and **TPS-Nf** as a photoacid generator (**PAG**) as an attractive single layer 157 nm photoresist.

2. Experimental

2.1. Materials

Dichloromethane was dried over CaH_2 and distilled from P_2O_5. α,α'-Azobis(isobutyronitrile) (**AIBN**) was recrystallized from methanol. Propylene glycol monomethyl ether acetate (**PGMEA**) was used as a casting solvent. Column chromatography was carried out using silica gel 60 (Merck 0.063-0.200 mm). Other reagents and solvents were used as received.

2.2. Synthesis of 2-chloroethanesulfonyl chloride [11]

Powdered phosphorus pentachloride (500 g, 2.4 mol) and dried sodium isethionate (100 g, 0.68 mol) were mixed, and the resulting solution was refluxed at 130 °C for 9 h. The solution was cooled to room temperature, poured on ice, and stirred in ice-water until unreacted phosphoryl chloride had completely reacted with water. The oil was separated, taken up in toluene, and dried over calcium chloride. After removing the solvent with a rotary evaporator, the residue was distilled to give 2-chloroethanesulfonyl chloride as colorless oil. Yield; 78 g (70%, 80-81 °C/10 mmHg) IR (KBr): ν 2992, 2935 ($-CH_2$), 1376 ($-SO_2Cl$) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.97-4.10 (m, 4H, $-CH_2-$) ppm. ^{13}C NMR (75 MHz $CDCl_3$) 35.9, 66.2 ppm.

2.3. Synthesis of 2-hydroxy-3-pinanyl vinyl sulfonate (VSO_3Pina) [8a]

To a 500 mL three-necked round-bottomed flask, equipped with a magnetic stirring bar, a dropping funnel, and a reflux condenser protected from moisture by a $CaCl_2$ drying tube were added 2-chloroethanesulfonyl chloride (4.90 g, 30.4 mmol), (1S,2S,3R,5S)-(+)-pinanediol (5.00 g, 29.4 mmol), and dichloromethane (50 mL). The flask was cooled with ice-water, and pyridine (5 mL, 65 mmol) was added to the well-cooled solution for 0.5 h through a dropping funnel under nitrogen flow. After the mixture was stirred at room temperature for 1.5 h, it was washed with a cold 10% aqueous Na_2CO_3 solution and water three times. The organic layer was separated, dried over magnesium sulfate, and concentrated under the reduced pressure. The product was purified by column chromatography (CH_2Cl_2 as an eluent). Yield 3.8g (51%). IR (KBr): ν 3536 (-OH), 3421($-CH_2-$), 1357($-SO_2-$), 1172, 983, 879 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ: 0.97 (s, 3H, $-CH_3$, *J*=9.9 Hz), 1.29 (s, 3H, $-CH_3$), 1.38 (d, 3H, $-CH_3$), 1.56 (d, 1H –CH<, J =9.9 Hz), 1.93-1.99 (m, 2H, -CH2-), 2.43 (tr, 1H, -CH2-, J=5.7 Hz), 2.22-2.30 (m, 1H, $-CH_2-$), 2.35 (s, 1H, -OH), 2.46-2.56 (m, 1H, $-CH_2-$), 4.91 (q, 1H, CH, J=9.9, J=5.7 Hz), 6.16 (d, 1H, $C\underline{H_c}H_b$- J_{ab}=16.8 Hz, J_{ac} =93.9 Hz), 6.47 (d, 1H, $CH_c\underline{H_b}$- J_{ab}=16.8 Hz, J_{ac} =93.9 Hz), 6.66 (dd, 1H, $=CH_a$, J_{ab}=16.8 Hz, J_{ac} =9.6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.9, 18.3, 28.9, 29.9, 36.0, 39.1, 41.0, 54.6, 74.2, 80.9, 130.5, 134.0 ppm. Anal. calc. for $C_{12}H_{20}O_4S$; C 55.36, H 7.74, S 12.32. Found: C 55.72, H 7.54, S 12.23.

2.4. Copolymerization of VSO_3Pina with HFISt

Typical procedure; **VSO_3Pina** (0.30 g, 1.2 mmol), **HFISt** (0.31g, 1.2mmol), and **AIBN** (8 mg, 0.048 mmol) were placed in a tube followed by several cycles of freeze and thaw. The tube was sealed and heated at 40 °C for 48 h. The polymerization mixture was transferred into a flask, and concentrated under the reduced pressure. The polymer was purified with dissolving in acetone and reprecipitation with hexane, and this was repeated in three times. The precipitate was collected, dissolved in acetone, poured into water, and dried in *vacuo* at 40 °C for 6h, giving the copolymer as a white powder. The yield was 0.2 g (33%). IR (KBr): ν 3400(O-H), 2931(C-H), 1334($-SO_3-$), 1214 (C-F) cm^{-1}

2.5. Lithographic evaluation

Resist films were prepared by casting a solution in **PGMEA** on silicone wafers. Pre-bake was performed at 100 °C for 60 sec. 4wt% **TPS-Nf** was used as a photoacid generator (**PAG**). Post exposure bake (**PEB**) was performed at 105°C for 60 sec. The 157-nm exposure was carried out with a F_2 laser exposure system. The resists were developed with 0.6 wt % aqueous **TMAH** solution at 25 °C for 60 sec.

2.6. Measurements

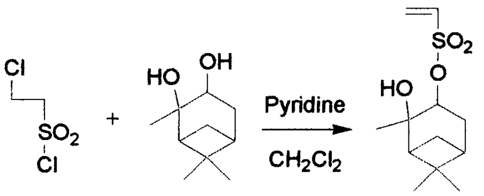
FT-IR spectra were measured with a Horiba FT-720 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a BRUKER DPX-300 spectrometer. Number- and weight-average molecular weights (M_n and M_w) were determined by a Tosoh HLC-8120 GPC system equipped with polystyrene gel columns (TSK GELs, GMH_{HR}-M and GMH_{HR}-L) at 40 °C in *N,N*-dimethylformamide (DMF) (containing 0.01 M of lithium bromide) at a flow rate of 1.0 mL/min. The optical density (**OD**) of resist films on MgF_2 substrate was measured with a F_2 laser exposure system VUVES-4500 (Litho Tech Japan). **VUV** spectra were measured on a VUV-200 (JASCO).

3. Results and discussion

3.1. Preparation of VSO_3Pina

VSO_3Pina was easily obtained by the reaction of 2-chloroethanesulfonyl chloride with (1S,2S,3R,5S)-(+)-pinanediol in the presence of pyridine as an acid acceptor (Scheme 1).

The structure of **VSO_3Pina** was determined by infrared, UV-visible, ^1H, ^{13}C NMR spectroscopy, and elemental analyses. The IR spectrum exhibited characteristic alcohol and sulfonyl ester absorptions at 3536 and 1357 cm^{-1}, respectively. Figure 1 shows the ^1H NMR spectrum of **VSO_3Pina**. The ^1H-NMR spectrum consists of two doublet and doublet-doublet signals for vinyl protons (δ =6.16, 6.47, and 6.66 ppm), a singlet for hydroxyl proton, and a quartet for a methine proton (δ = 4.91 ppm) adjacent to oxygen. Elemental analysis showed very good agreement with calculated values.



Scheme 1

$VnSO_3Pina$

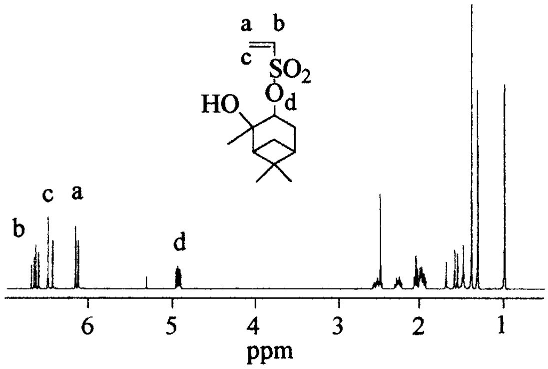


Fig. 1. ^1H NMR spectra of **VSO_3Pina** in $CDCl_3$.

3.2. Copolymerization of VSO_3Pina with HFISt

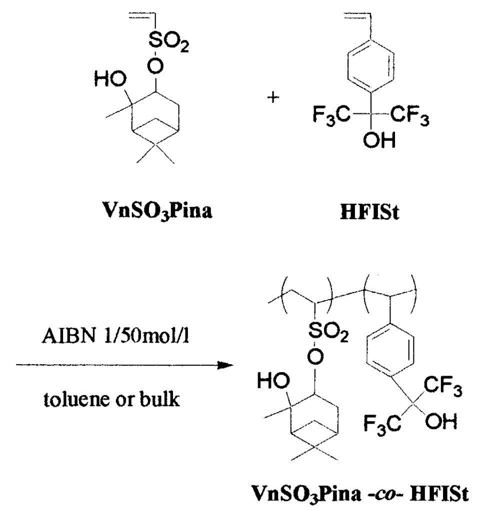
Free radical copolymerization of **VSO_3Pina** 0.3 g (1.2 mmol) with **HFISt** 0.31 g (1.2 mmol) was carried out in bulk using an equimolar ratio of **VSO_3Pina** and **HFISt** at 40 °C for 48 h in the presence of **AIBN** 8 mg (0.047 mmol) as a radical initiator (Scheme 2, run 1 in Table 1).

Polymerization proceeded smoothly, giving the high molecular weight copolymer (white powder). A molar ratio of **VSO_3Pina** and **HFISt** in the copolymer determined by a sulfur analysis was 23 mol% and 73 mol%, respectively. The M_n of the copolymer was 190,000, which is excessively high for the use of photoresist materials. Thus, solution polymerizations were then investigated to obtain lower M_n copolymers. In addition, since the dissolution rate of the copolymer was too high, the higher molar ratio of

Table 1 Copolymerimerization of VSO3Pina with HFISt a)

Run	feed ratio b)	conc. [mol/l]	Mn c)	Mw/Mn c)	copolymer composition (**VSO_3Pina** : **HFISt**)	Yield [%]
1	1	bulk	190000	3.37	23 : 73	30
2	5	1	26000	1.27	45 : 55	27
3	10	2	22900	1.49	73 : 27	33
4	10	1	16800	1.37	77 : 23	12

a) 40°C 48h b) Monomer feed ratio of **VSO_3Pina** to **HFISt** c) Detected by GPC (PSt standards DMF)



Scheme 2

VSO_3Pina in the copolymer is required to decrease the solubility to aqueous **TMAH** solution. When the monomer feed ratio of **VSO_3Pina** and **HFISt** was 5:1, the copolymer composition ratio of **VSO_3Pina** (45 mol%) and **HFISt** (55 mol%) was obtained (run 2). On the other hand, the copolymer composition of **VSO_3Pina** (73 mol%) and **HFISt** (27 mol%) was obtained when the monomer feed ratio of **VSO_3Pina** and **HFISt** was 10:1 (run 3). The resulting poly(**VSO_3Pina_{73}**-*co*-**$HFISt_{27}$**) was almost insoluble in 0.6 wt% aqueous **TMAH** solution. Thus, the appropriate feed ratio of **VSO_3Pina** and **HFISt** was determined as 10:1. Under the 1 mol/L monomer concentration, the M_n of the copolymer was reduced to 16,800 (run 4).

Copolymers were identified as the expected poly(**VSO_3Pina**-*co*-**HFISt**)s by IR and ^1H NMR spectroscopy, and elemental analysis. The IR spectrum of the poly(**VSO_3Pina**-*co*- **HFISt**) exhibited a characteristic O-H bond stretching at 3400 cm^{-1} and a sulfonate stretching at 1334 cm^{-1}. In the ^1H NMR spectrum, the vinyl protons of **VSO_3Pina** and **HFISt** at around 6.5 ppm completely disappeared.

Transparent films were prepared by spin-casting a **PGMEA** solution of poly(**VSO_3Pina**-*co*-**HFISt**)s on a silicon. The transmittance of the resulting poly(**VSO_3Pina_{73}**-*co*-**$HFISt_{27}$**) film was measured with a **VUV** spectrophotometer and it was found that poly(**VSO_3Pina_{73}**-*co*-**$HFISt_{27}$**) film was quite transparent at 157 nm.

3.3. Lithographic Evaluation

A preliminary formulation was made by dissolving poly(**VSO_3Pina_{73}**-*co*-**$HFISt_{27}$**) and 4 wt% **TPS-Nf** as a **PAG** in **PGMEA**. The resist film showed an **OD** value of 3.6 μm^{-1}. Lithography characteristics were studied using a F_2 laser exposure system "VUVES-4500" (LithoTech Japan). The sensitivity curve as shown in Figure 2 indicates that the sensitivity and contrast are 10 mJ cm^{-2} and 6, respectively, when a 120 nm-thick resist film pre-baked at 100 °C for 60 sec was exposed to 157-nm laser, post-baked at 105 °C for 60 sec, and followed by developed with 0.6 wt% aqueous **TMAH** solution. The 2-hydroxy-3-pinanyl sulfonate group is responsible for photo-acidolysis, giving an alkaline developable sulfonic acid (Scheme 3).

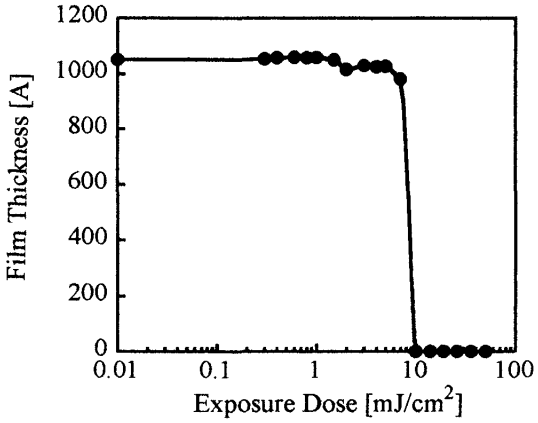
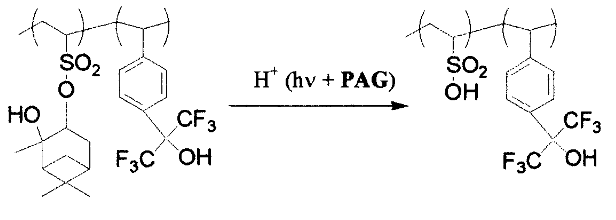


Fig. 2. Film thickness change of poly(**VSO_3Pina**-*co*-**HFISt**) film with 4% **PAG**.



Scheme 3

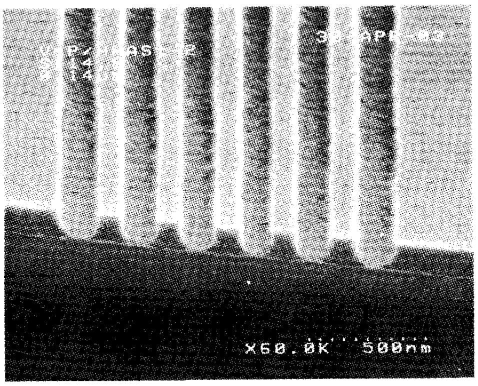


Fig. 3. 140nm lines and spaces pattern of the resist consisting of poly(**VSO_3Pina_{73}**-co-**$HFISt_{27}$**) and **TPS-Nf** by F2 laser contact exposure. Resist thickness: 120 nm. Exposure dose: 14.8mJ/cm^2. Substrate: 40nm-thick BARC for KrF (Brewer's "DUV-30J").

A 140 nm lines and spaces pattern that was minimum pattern size on the mask was obtained in a 120 nm- thick film using a 0.6wt% **TMAH** aqueous solution by F2 laser contact exposure (Fig. 3). This result indicates the poly(**VSO$_3$Pina**$_{73}$-*co*-**HFISt**$_{27}$) would work as a high-sensitive and high-contrast resist platform.

4. Conclusion

A Novel copolymer from **VSO$_3$Pina** and **HFISt** was prepared by free radical polymerization, in which the **VSO$_3$Pina** unit was responsible for the polarity change and the **HFISt** unit for the alkaline solubility. The poly(**VSO$_3$Pina**$_{73}$-*co*-**HFISt**$_{27}$) showed a low **OD** of 3.6 μm^{-1}. The resist system based on the poly(**VSO$_3$Pina**$_{73}$-*co*-**HFISt**$_{27}$) and **TPS-Nf** showed a high sensitivity of 10 mJ cm^{-2} and a contrast of 6 as a 157 nm resist, and its OD was 3.6. This resist showed a high resolution of 140 nm by F2 laser contact exposure.

References

1. W. Wakamiya *SEMI Technology Symposium*
2002 Poceedings 1-11.
2. H. Ito, G. M. Wallraff, N. Fender, P. J. Brock,
W. D. Hinsberg, A. Mahorowala, C. E. Larson,
H. D. Truong, G. Breyta, R. D. Allen. *J. Vac.*
Sci. Technol. **2001**, *B, 19*, 2678.
3. H. Ito, G. M. Wallraff, N. Fender, P. J. Brock,
W. D. Hinsberg, A. Mahorowala, C. E. Larson,
H. D. Truong, G. Breyta, R. D. Allen, *J. Vac.*
Sci. Technol. **2001**, *19*, 2678.
4. a) R. R. Dammel, R. Sakamuri, T. Kudo, A.
Romano, L. Rhodes, R. Vicari, C. Hacker, W.
Conley, D. Miller, *J. Photopolym. Sci. Technol.*
2001, *14*, 603. b) H. V. Tran, R. J. Hung, T.
Chiba, S. Yamada, T. Mrozek, Y. Hsieh, C. R.
5. Chambers, B. P. Osborn, B. C. Trinque, M. J.
Pinnow, S. A. MacDonald, C. G. Willson, D. P.
6. Sanders, E. F. Connor, R. H. Grubbs, W.
Conley *Macromolecules* **2002**, *35*, 6539.
7. a) D. Schmaljohann, Y. C. Bae, J. Dai, G. L.
Weibel, A. H. Hamad, C. K. Ober, *Proc. SPIE*
8. **2000**, *3999*, 330. b) M. Toriumi, I. Satou, T.
Itani, *J. Vac. Sci. Technol.* **2000**, *18*, 3328.
T. H. Fedynyshyn, R. R. Kunz, R. Sinta, M.
Sworin, W. Mowers, R. B. Goodman, S. P.
Doran, *Proc. SPIE.* **2001**, *4345*, 298. d) K. Y.
Song, K. S. Yoon, S. J. Choi, S. G. Woo, W.
S.Han, J. J. Lee, S. K. Lee, C. H. Noh, K.
Honda, *Proc. SPIE.* **2002**, *4690*, 504. e) T.
Naito, S. Saito, N. Shida, T. Ushirogouchi, *J.*
Photopolym. Sci. Technol. **2002,** *15*, 689.
9. W. Conley, D. Miller, C. Chambers, B. C.
Trinque, B. Osborn, T. Chiba, P. Zimmerman,
R. Dammel, A. Romano, C. G. Willson, *J.*
Photopolym. Sci. Technol. **2002**, *15*, 613.
10. a) S. Ando, T. Fujigaya, M. Ueda, *Jpn. J. Appl.*
Phys. **2002**, *41, 2A,* L105. b) S. Ando, T.
Fujigaya, M. Ueda, *J. Photopolym. Sci.*
Technol. **2002**, *15*, 559.
11. a) T. Fujigaya, Y. Shibasaki, S. Ando, S.
Kishimura, M. Endo, M. Sasago, and M. Ueda,
Chem. Mater. **2003**, *15*, 1512. b) T. Fujigaya,
Y. Shibasaki, S. Ando, S. Kishimura, M. Endo,
M. Sasago, and M. Ueda. *J. Photopolym. Sci.*
Technol. **2002**, *15*, 694.
12. a) T. Ohfuji, M. Takahashi, M. Sasago, S.
Noguchi, K. Ichimura, *J. Photopolym. Sci.*
Technol. **1997**, *10*, 551. b) K. Ichimura, K.
Arimitsu, S. Noguchi, T. Ohfuji, T. Naito,
Polym. Mater. Sci. Eng. **1999**, *63*, 81. c) S. W.
Park, K. Arimitsu, K. Ichimua, T. Ohfuji, *J.*
Photopolym. Sci. Technol. **1999**, *12*, 293.
13. S. W. Park, K. Arimitsu, S. Lee, and K.
Ichimura. *Chem. Lett.* **2000**, *29*, 1036.
14. A. A Goldberg, *J. Chem. Soc.* **1945**, 464.