

Synthesis and Properties of Fluorine-containing Poly(ether)s with Pendant Hydroxyl Groups by the Polyaddition of Bis(oxetane)s and Bisphenol AF

Yousuke KONNO, Hidehiro SUZUKI, Hiroto KUDO, Atsushi KAMEYAMA, and Tadatomi NISHIKUBO[†]

*Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*

(Received August 4, 2003; Accepted November 26, 2003)

ABSTRACT: Fluorine-containing poly(ether)s with pendant primary hydroxyl groups were synthesized by the polyaddition of bisphenol AF di(3-ethyl-3-oxetanylmethyl ether) (BPAFEO) with bisphenol AF (BPAF) using quaternary onium salts, crown ether complexes or organic bases as catalysts. When the polyaddition was performed with co-catalysts such as tetraphenylphosphonium chloride (TPPC) and 1,8-diazabicyclo[5.4.0]undecene-7 (DBU) without solvent at 190 °C for 120 h, the corresponding poly(ether)s pendant primary hydroxyl groups were successfully obtained in good yield. The polyaddition of various bis(oxetane)s with BPAF also proceeded in bulk to provide the corresponding poly(ether)s. It was found that these poly(ether)s are highly transparent at 157 nm, and transmittance of poly(ether)s were determined to be 34–55 % at 157 nm for 0.1 μm thickness.

KEY WORDS Polyaddition / Bis(oxetane) / Synthesis / Fluorine-containing Poly(ether)s / High Transparency at 157 nm /

It is well known that fluorine-containing polymers exhibit high thermal stability, excellent chemical resistance, and many other special properties. Therefore, fluoropolymers have been investigated as high performance materials for application of optical and microelectronics derivatives. Recently, most research groups investigated fluoropolymers as photoresist materials for F₂ lithography because they are fairly transparent in the vacuum ultraviolet (VUV).^{1–6}

In our recent paper, we demonstrated the synthesis and characterization of fluorine-containing polymers by the polyaddition of fluorine-containing bis(epoxide)s with fluorine-containing dicarboxylic acids, diols,⁷ and active diesters.⁸ The refractive indices of the obtained polymers decreased when the fluorine contents increased. In addition, it was found that fluorine-containing poly(ether)s with pendant hydroxyl groups are highly transparent at 157 nm, and transmittance of poly(ether)s were determined to be 14–75 % at 157 nm for 0.1 μm thickness.⁹

Meanwhile, our research group previously reported the polyaddition of bis(oxetane)s with various protonic reagents such as dicarboxylic acids,¹⁰ dithiols,¹¹ and bis(phenol)s¹² proceeded smoothly in the presence of quaternary onium salts and crown ether complexes as catalysts to give corresponding soluble polymers with pendant primary hydroxyl groups. The pendant primary hydroxyl groups seemed to be useful reactive groups for chemical modification.

In this article, we report synthesis and properties of fluorine-containing poly(ether)s with pendant primary hydroxyl groups by the polyaddition of fluorine-con-

taining bis(oxetane)s with bisphenol AF. Furthermore, we investigated on the chemical modification of fluoropolymers with pendant primary hydroxyl groups.

EXPERIMENTAL

Materials

Solvents were dried using P₂O₅, CaH₂, or Na metal wire, and purified in the usual way before use. Tetra-butylammonium bromide (TBAB) was recrystallized twice from ethyl acetate. Reagent grades of tetraphenylphosphonium bromide (TBPB), tetraphenylphosphonium chloride (TPPC), tetraphenylphosphonium iodide (TPPI), 18-crown-6 (18-C-6), potassium chloride (KCl), potassium bromide (KBr), potassium iodide (KI), cesium carbonate (Cs₂CO₃), and potassium hydroxide (KOH) were used without further purification. 3-Chloromethyl-3-ethyl-oxetane (CMEO) (donated from Toagosei Co., Ltd.) was purified by distillation. (3-Methyloxetane-3-yl)methyl 4-toluenesulfonate (MOMT) was synthesized in a 53 % yield according to a reported method.¹³ BPAF was purified by sublimation. 1,3-Bis(hexafluorohydroxyisopropyl)benzene (1,3-HFAB) was purified by distillation. 1,4-Bis(hexafluorohydroxyisopropyl)cyclohexane (1,4-HFAC) (donated from JSR Co., Ltd.) was purified by distillation. *tert*-Butyl bromoacetate (BBAc) was used without further purification.

Measurements

Melting points were determined with a Yanako MP-500D hot-stage microscope. Infrared (IR) spectra

[†]To whom correspondence should be addressed (E-mail: nishit02@kanagawa-u.ac.jp).

were measured on a Jasco Model IR-420 spectrometer. The ^1H NMR spectra were recorded on JEOL Model JNM α -500 (500 MHz for ^1H NMR, 125 MHz for ^{13}C NMR, 470 MHz for ^{19}F NMR) instruments in CDCl_3 using Me_4Si (TMS) for ^1H NMR and C_6F_6 for ^{19}F NMR as an internal standard. The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymers were estimated by gel permeation chromatography (GPC) with the use of a Tosoh model HLC-8220 GPC equipped with refractive index and ultraviolet detectors using TSK gel columns (eluent DMF, calibrated with narrow molecular weight polystyrene standards). The T_g s of the polymer were measured on a Seiko Instruments differential scanning calorimeter (DSC) Model EXSTAR6000/DSC6200 at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. The thermal analysis was performed on a Seiko Instruments thermogravimetric analysis (TGA) Model EXSTAR6000/TG/DTA6200 at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. Elemental analysis was measured on a Perkin Elmer PE2400 series II CHNS/O analyzer. Vacuum ultraviolet (VUV) spectra were measured on a Jasco Model VU-201.

Synthesis of Bisphenol AF di(3-ethyl-3-oxetanylmethyl)ether (BPAFEO)

NMP solution (100 mL) of BPAF (16.81 g, 50 mmol), KOH (9.90 g, 150 mmol), and TBAB (1.61 g, 5 mol%) were stirred for 1 h at 90°C . Then, CME0 (20.31 g, 150 mmol) was added to the solution, and the mixture was stirred for 3 h at the same temperature. The reaction mixture was diluted in ethyl acetate, washed three times with water, and dried with anhydrous MgSO_4 . Excess CME0 and the solvent were evaporated, and then the crude product was purified by alumina column chromatography with ethyl acetate/*n*-hexane (1/5) as an eluent. The yield of BPAFEO was 24.74 g (93%). Mp: $131.2\text{--}132.1^\circ\text{C}$. IR (KBr, cm^{-1}): 2965, 2935, 2872 ($\nu\text{C-H}$), 1611, 1515 ($\nu\text{C=C}$, aromatic), 1297, 1027 ($\nu\text{C-O-C}$, ether), 1254, 1206, 1173 ($\nu\text{C-F}$), 983 ($\nu\text{C-O-C}$, cyclic ether). ^1H NMR (500 MHz, $\text{DMSO-}d_6$, TMS): δ 0.90 (t, $J = 7.3$ Hz, 6.0H, $-\text{CH}_3$), 1.80 (q, $J = 7.3$ Hz, 4.0H, CH_2), 4.14 (s, 4.0H, O-CH_2), 4.35 (d, $J = 5.5$ Hz, 4.0H, CH_2 in oxetane), 4.45 (d, $J = 5.5$ Hz, 4.0H, CH_2 in oxetane), 7.10 (d, $J = 9.0$ Hz, 4.0H, aromatic H), 7.26 ($J = 9.0$ Hz, 4.0H, aromatic H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, TMS): δ 8.01 (CH_3), 26.18 (CH_2), 42.38 (C in oxetane ring), 63.01 (C in BPAF), 70.13 (O-CH_2), 76.66 (CH_2 in oxetane ring), 124.21 (q, $J = 283.8$ Hz, CF_3), 114.57, 124.34, 130.97, 159.07 (aromatic C). ^{19}F NMR (470 MHz, $\text{DMSO-}d_6$, C_6F_6): δ -62.4 (s, CF_3). Anal. Calcd for $\text{C}_{27}\text{H}_{30}\text{F}_6\text{O}_4$: C, 60.90%; H, 5.68%. Found: C, 61.08%; 5.73%.

Synthesis of bisphenol AF di(3-methyl-3-oxetanylmethyl)ether (BPAFMO)

The reaction was carried out with BPAF (0.841 g, 2.5 mmol) and MOMT (2.563 g, 10 mmol) in NMP (10 mL) using KOH (0.495 g, 7.5 mmol), and TBAB (0.081 g, 5 mol%) by the same way for the synthesis of BPAFEO.

The yield of BPAFEO was 1.019 g (85%). Mp: $110.2\text{--}111.1^\circ\text{C}$. IR (KBr, cm^{-1}): 2961, 2935, 2871 ($\nu\text{C-H}$), 1611, 1516 ($\nu\text{C=C}$, aromatic), 1299, 1040 ($\nu\text{C-O-C}$, ether), 1254, 1206, 1173 ($\nu\text{C-F}$), 980 ($\nu\text{C-O-C}$, cyclic ether). ^1H NMR (500 MHz, $\text{DMSO-}d_6$, TMS): δ 1.37 (s, 6.0H, $-\text{CH}_3$), 4.09 (s, 4.0H, O-CH_2), 4.32 (d, $J = 5.5$ Hz, 4.0H, CH_2 in oxetane), 4.51 (d, $J = 5.5$ Hz, 4.0H, CH_2 in oxetane), 7.09 (d, $J = 9.0$ Hz, 4.0 H, aromatic H), 7.26 (d, $J = 9.0$ Hz, 4.0 H, aromatic H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, TMS): δ 20.88 (CH_3), 38.92 (C in oxetane ring), 63.03 (C in BPAF), 72.40 (O-CH_2), 72.47 (CH_2 in oxetane ring), 124.19 (q, $J = 286.3$ Hz, CF_3), 114.53, 124.32, 130.95, 159.08 (aromatic C). ^{19}F NMR (470 MHz, $\text{DMSO-}d_6$, C_6F_6): δ -62.3 (s, CF_3). Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{F}_6\text{O}_4$: C, 59.52%; H, 5.19%. Found: C, 59.41%; 5.16%.

Synthesis of 1,3-Bis(hexafluorohydroxyisopropyl)benzene di(3-ethyl-3-oxetanylmethyl)ether (1,3-HFABEO)

1,3-HFABEO was synthesized by the reaction of 1,3-HFAB (6.152 g, 15 mmol) with CME0 (8.077 g, 60 mmol) using KOH (3.960 g, 60 mmol), and TBAB (0.484 g, 5 mol%) in NMP (100 mL) for 24 h by the same way for the synthesis of BPAFEO. The yield of 1,3-HFABEO was 8.103 g (89%). Mp: $58.6\text{--}59.5^\circ\text{C}$. IR (KBr, cm^{-1}): 2969, 2942, 2879 ($\nu\text{C-H}$), 1482, 1464 ($\nu\text{C=C}$, aromatic), 1281, 1029, 1012 ($\nu\text{C-O-C}$, ether), 1264, 1220, 1169, 1130 ($\nu\text{C-F}$), 987 ($\nu\text{C-O-C}$, cyclic ether). ^1H NMR (500 MHz, $\text{DMSO-}d_6$, TMS): δ 0.90 (t, $J = 7.5$ Hz, 6.0H, $-\text{CH}_3$), 1.77 (q, $J = 7.5$ Hz, 4.0H, CH_2), 3.75 (s, 4.0H, O-CH_2), 4.34 (d, $J = 6.3$ Hz, 4.0H, CH_2 in oxetane), 4.41 (d, $J = 6.3$ Hz, 4.0H, CH_2 in oxetane), 7.75 (s, 1.0H, aromatic H), 7.86 (d, $J = 8.0$ Hz, 2.0H, aromatic H), 7.93 (t, $J = 8.0$ Hz, 1.0H, aromatic H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, TMS): δ 7.68 (CH_3), 25.73 (CH_2), 42.74 (C in oxetane ring), 68.80 (O-CH_2), 76.04 (CH_2 in oxetane ring), 81.80 ($\text{Ar-C}(\text{CF}_3)_2\text{-O}$), 122.08 (q, $J = 287.5$ Hz, CF_3), 126.79, 127.83, 130.49, 130.80 (aromatic C). ^{19}F NMR (470 MHz, $\text{DMSO-}d_6$, C_6F_6): δ -68.8 (s, CF_3). Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{F}_{12}\text{O}_4$: C, 47.53%; H, 4.32%. Found: C, 47.66%; 4.36%.

Synthesis of 1,3-Bis(hexafluorohydroxyisopropyl)benzene di(3-methyl-3-oxetanylmethyl)ether (1,3-HFABMO)

The reaction of 1,3-HFAB (2.051 g, 5 mmol) with MOMT (5.126 g, 20 mmol) was carried out using KOH (1.122 g, 20 mmol), and TBAB (0.161 g, 5 mol%) in NMP (20 mL) for 24 h by the same way for the synthesis of BPAFEO.

The yield of 1,3-HFABMO was 8.103 g (89 %). Mp: 58.6–59.5 °C. IR (KBr, cm^{-1}): 2967, 2877 ($\nu\text{C-H}$), 1492, 1479, 1465, 1456 ($\nu\text{C=C}$, aromatic), 1282, 1037 ($\nu\text{C-O-C}$, ether), 1264, 1219, 1170, 1130 ($\nu\text{C-F}$), 986 ($\nu\text{C-O-C}$, cyclic ether). $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$, TMS): δ 1.36 (s, 6.0H, $-\text{CH}_3$), 3.71 (s, 4.0H, O-CH_2), 4.30 (d, $J = 6.0$ Hz, 4.0H, CH_2 in oxetane), 4.44 (d, $J = 6.0$ Hz, 4.0H, CH_2 in oxetane), 7.73 (s, 1.0H, aromatic H), 7.86 (d, $J = 8.0$ Hz, 2.0H, aromatic H), 7.91 (t, $J = 8.0$ Hz, 1.0H, aromatic H). $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$, TMS): δ 20.32 (CH_3), 39.50 (C in oxetane ring), 70.82 (O-CH_2), 78.05 (CH_2 in oxetane ring), 81.75 ($\text{Ar-C}(\text{CF}_3)_2\text{-O}$), 122.01 (q, $J = 290.0$ Hz, CF_3), 126.81, 127.70, 130.48, 130.76 (aromatic C). $^{19}\text{F NMR}$ (470 MHz, $\text{DMSO-}d_6$, C_6F_6): δ -68.8 (s, CF_3). *Anal.* Calcd for $\text{C}_{24}\text{H}_{26}\text{F}_{12}\text{O}_4$: C, 45.68 %; H, 3.83 %. Found: C, 45.59 %; 3.75 %.

Synthesis of 1,4-Bis(hexafluorohydroxyisopropyl)cyclohexane di(3-ethyl-3-oxetanylmethyl)ether (1,4-HFACEO)

1,4-HFACEO was prepared by the reaction of 1,4-HFAC (2.081 g, 5 mmol) with CMEO (2.692 g, 20 mmol) using KOH (1.122 g, 20 mmol), and TBAB (0.161 g, 5 mol%) in NMP (20 mL) for 48 h by the same way for the synthesis of BPAFEO. The yield of 1,3-HFACEO was 2.106 g (69 %). Mp: 75.8–76.7 °C. IR (KBr, cm^{-1}): 2967, 2940, 2879 ($\nu\text{C-H}$), 1272, 1044 ($\nu\text{C-O-C}$, ether), 1213, 1141, 1113 ($\nu\text{C-F}$), 983 ($\nu\text{C-O-C}$, cyclic ether). $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$, TMS): δ 0.87 (t, $J = 7.5$ Hz, 6.0H, $-\text{CH}_3$), 1.30–2.73 (m, 14.0H, CH_2 , CH_2 , CH in cyclohexane ring), 3.79 (d, $J = 9.0$ Hz, 2.0H, CH_2 in oxetane), 3.84 (d, $J = 9.0$ Hz, 2.0H, CH_2 in oxetane), 4.30 (s, 4.0H, O-CH_2). $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$, TMS): δ 7.67 (CH_3), 24.84, 26.04, 26.59, 37.10 (C in cyclohexane ring), 25.65 (CH_2), 42.63 (C in oxetane ring), 67.19 (O-CH_2), 76.19 (CH_2 in oxetane ring), 81.70–81.95 ($\text{Ar-C}(\text{CF}_3)_2\text{-O}$), 122.87 (q, $J = 289.9$ Hz, CF_3). $^{19}\text{F NMR}$ (470 MHz, $\text{DMSO-}d_6$, C_6F_6): δ -66.5 (q, $J = 9.4$ Hz, 6.0H, CF_3), -66.1 (q, $J = 9.4$ Hz, 6.0H, CF_3). *Anal.* Calcd for $\text{C}_{24}\text{H}_{32}\text{F}_{12}\text{O}_4$: C, 47.06 %; H, 5.27 %. Found: C, 47.30 %; 5.33 %.

Synthesis of 1,4-Bis(hexafluorohydroxyisopropyl)cyclohexane di(3-methyl-3-oxetanylmethyl)ether (1,4-HFACMO)

1,4-HFACMO was obtained in a 63 % yield by the reaction of 1,4-HFAC (2.081 g, 5 mmol) with MOMT (5.126 g, 20 mmol) using KOH (1.122 g, 20 mmol), and TBAB (0.161 g, 5 mol%) in NMP (20 mL) for 48 h by the same way for synthesis of BPAFEO. The yield of 1,4-HFABMO was 8.103 g (63 %). Mp: 85.6–86.5 °C. IR (KBr, cm^{-1}): 2965, 2940, 2877 ($\nu\text{C-H}$), 1273, 1047 ($\nu\text{C-O-C}$, ether), 1213, 1142, 1113 ($\nu\text{C-F}$), 984 ($\nu\text{C-O-C}$, cyclic ether). $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$, TMS): δ 1.27 (s, 6.0H, $-\text{CH}_3$), 1.30–2.69 (m, 10.0H, CH_2 , CH in cyclohexane), 3.75 (d, $J = 9.0$ Hz, 4.0H, CH_2 in oxetane), 3.78 (d, $J = 9.0$ Hz, 4.0H, CH_2 in oxetane), 4.30 (s, 4.0H, O-CH_2). $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$, TMS): δ 20.30 (CH_3), 24.97, 26.01, 26.49, 37.12 (C in cyclohexane), 40.01 (C in oxetane ring), 69.41 (O-CH_2), 78.03 (CH_2 in oxetane ring), 81.50–82.40 ($\text{Ar-C}(\text{CF}_3)_2\text{-O}$), 122.92 (q, $J = 289.9$ Hz, CF_3). $^{19}\text{F NMR}$ (470 MHz, $\text{DMSO-}d_6$, C_6F_6): δ -66.5 (d, $J = 8.9$ Hz, CF_3), -66.3 (d, $J = 8.9$ Hz, CF_3). *Anal.* Calcd for $\text{C}_{22}\text{H}_{28}\text{F}_{12}\text{O}_4$: C, 45.21 %; H, 4.83 %. Found: C, 45.41 %; 4.80 %.

Typical Procedure for the synthesis of Polymer 1 by the polyaddition of BPAFEO with BPAF

A typical procedure for the polyaddition of BPAFEO with BPAF was as follows: TPPC (9.4 mg, 5 mol%) was dried in a glass tube *in vacuo* at 60 °C for 5 h prior to use. BPAFEO (266.3 mg, 0.5 mmol), BPAF (168.1 mg, 0.5 mmol), and DBU (3.8 mg, 5 mol%) as a catalyst were charged into a glass tube in a dry box, after which the tube was evacuated and then sealed using a gas torch. The reaction was performed at 190 °C for 120 h in the sealed tube under stirring, then the solution was diluted with ethyl acetate, washed three times with minimal amounts of water to remove the catalyst, and dried with anhydrous MgSO_4 . The solvent evaporated, and poured into diethyl ether/*n*-hexane (1/5) to precipitate the polymer. The resulting polymer was reprecipitated from THF into diethyl ether/*n*-hexane (1/5), and dried *in vacuo*. The yield of resulting polymer (polymer **1**) was 0.366 g (87 %). The number-average molecular weight (M_n) of the polymer determined by GPC was 8200 ($M_w/M_n = 2.61$). IR (film, cm^{-1}): 3396 ($\nu\text{O-H}$), 2968, 2938, 2883 ($\nu\text{C-H}$), 1612, 1515 ($\nu\text{C=C}$, aromatic), 1252, 1023 ($\nu\text{C-O-C}$, ether), 1206, 1192, 1173 ($\nu\text{C-F}$). $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$, TMS): δ 0.82–1.13 (m, 3.0H, CH_3), 1.37–1.57 (m, 2.0H, CH_2), 3.53–4.13 (m, 6.0H, $\text{C-CH}_2\text{-O}$), 4.75 (brs, 0.8H, OH), 6.84–7.21 (m, 8.0H, aromatic H). $^{19}\text{F NMR}$ (470 MHz, $\text{DMSO-}d_6$, C_6F_6): δ -62.4 (s,

CF₃). *Anal.* Calcd for C₂₁H₂₀F₆O₃: C, 58.01%; H, 4.64%. Found: C, 57.95%; H, 4.52%.

Synthesis of polymer 2 by the polyaddition of BPAF-MO with BPAF

The reaction was carried out with BPAFMO (252.2 mg, 0.5 mmol) and BPAF (168.1 mg, 0.5 mmol) using TBPC (9.4 mg, 5 mol%) and DBU (3.8 mg, 5 mol%) as co-catalysts without solvent at 190 °C for 72 h. The yield of polymer **2** was 0.391 g (93%). The M_n of the polymer **2** determined by GPC was 9100 ($M_w/M_n = 4.67$). IR (film): 3412 (ν O-H), 2972, 2937, 2877 (ν C-H), 1612, 1516 (ν C=C, aromatic), 1298, 1051 (ν C-O-C, ether), 1253, 1206, 1192, 1173 (ν C-F). ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 0.80–1.79 (m, 3.0H, CH₃), 3.34–3.95 (m, 6.0H, C-CH₂-O), 4.81 (brs, 0.8H, OH), 6.81–7.23 (m, 8.0H, aromatic H). ¹⁹F NMR (470 MHz, DMSO-*d*₆, C₆F₆): δ -62.6 (s, CF₃).

Synthesis of polymer 3 by the polyaddition of 1,3-HFA-BEO with BPAF

Polymer **3** was synthesized by the polyaddition of 1,3-HFABEO (303.2 mg, 0.5 mmol) with BPAF (168.1 mg, 0.5 mmol) using TPPC (9.4 mg, 5 mol%) and DBU (3.8 mg, 5 mol%) as a co-catalyst without solvent at 190 °C for 120 h. The yield of polymer **3** was 0.185 g (40%). The M_n of polymer **3** determined by GPC was 10700 ($M_w/M_n = 1.80$). IR (film, cm⁻¹): 3427 (ν O-H), 2975, 2880 (ν C-H), 1613, 1584, 1517, 1473 (ν C=C, aromatic), 1328, 1032 (ν C-O-C, ether), 1256, 1220, 1208, 1173, 1150, 1133 (ν C-F). ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 0.83–0.95 (m, 6.0 H, CH₃), 1.52–1.70 (m, 4.0H, CH₂), 3.32–3.89 (m, 12.0H, C-CH₂-O), 4.78 (brs, 1.5H, OH), 6.82–7.21 (m, 8.0 H, aromatic H), 7.56–7.75 (m, 4.0H, aromatic H). ¹⁹F NMR (470 MHz, DMSO-*d*₆, C₆F₆): δ -68.9 (s, 12.0 F, CF₃), -62.6 (s, 6.0 F, CF₃).

Synthesis of polymer 4 by the polyaddition of 1,3-HFABMO with BPAF

The polyaddition of 1,3-HFABMO (282.2 mg, 0.5 mmol) with BPAF (168.1 mg, 0.5 mmol) was carried out using TPPC (9.4 mg, 5 mol%) and DBU (3.8 mg, 5 mol%) as a co-catalysts without solvent at 190 °C for 72 h. The yield of polymer **4** was 0.344 g (77%). The M_n of polymer **4** determined by GPC was 10500 ($M_w/M_n = 2.09$). IR (film, cm⁻¹): 3427 (ν O-H), 2975, 2880 (ν C-H), 1613, 1584, 1517, 1473 (ν C=C, aromatic), 1327, 1032 (ν C-O-C, ether), 1256, 1220, 1208, 1173, 1150, 1133 (ν C-F). ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 0.84–1.95 (m, 6.0H, CH₃), 3.32–3.89 (m, 12.0H, C-CH₂-O), 4.83 (brs, 1.7H, OH), 6.83–7.21 (m, 8.0H, aromatic H), 7.64–

7.76 (m, 4.0H, aromatic H). ¹⁹F NMR (470 MHz, DMSO-*d*₆, C₆F₆): δ -69.0 (s, 12.0F, CF₃), -62.6 (s, 6.0F, CF₃).

Synthesis of polymer 5 by the polyaddition of 1,4-HFACEO with BPAF

Polymer **5** was prepared by the polyaddition of 1,4-HFACEO (306.2 mg, 0.5 mmol) with BPAF (168.1 mg, 0.5 mmol) using TPPC (9.4 mg, 5 mol%) and DBU (3.8 mg, 5 mol%) as a co-catalysts without solvent at 190 °C for 120 h. The yield of polymer **5** was 0.192 g (40%). The M_n of polymer **5** determined by GPC was 10800 ($M_w/M_n = 1.89$). IR (film, cm⁻¹): 3409 (ν O-H), 2969, 2886 (ν C-H), 1613, 1517 (ν C=C, aromatic), 1328, 1040 (ν C-O-C, ether), 1255, 1208, 1174, 1137, 1115 (ν C-F). ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 0.84–1.95 (m, 20.0H, CH₃, CH₂, CH₂, CH in cyclohexane), 3.32–3.82 (m, 12.0H, C-CH₂-O), 4.66 (brs, 1.9H, OH), 6.82–7.19 (m, 8.0H, aromatic H). ¹⁹F NMR (470 MHz, DMSO-*d*₆, C₆F₆): δ -67.0 to -65.9 (m, 12.0F, CF₃), -62.6 (s, 6.0F, CF₃).

Synthesis of polymer 6 by the polyaddition of 1,4-HFACMO with BPAF

The reaction of 1,4-HFACMO (292.2 mg, 0.5 mmol) with BPAF (168.1 mg, 0.5 mmol) was carried out using TPPC (9.4 mg, 5 mol%) and DBU (3.8 mg, 5 mol%) as a co-catalysts without solvent at 190 °C for 72 h. The yield of polymer **6** was 0.381 g (83%). IR (film): 3400 (ν O-H), 2959, 2884 (ν C-H), 1613, 1517 (ν C=C, aromatic), 1328, 1046 (ν C-O-C, ether), 1255, 1208, 1174, 1137, 1115 (ν C-F). ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 0.82–1.94 (m, 16.0 H, CH₃, CH₂, CH in cyclohexane), 3.31–3.80 (m, 12.0H, C-CH₂-O), 4.73 (brs, 1.8H, OH), 6.82–7.19 (m, 8.0H, aromatic H). ¹⁹F NMR (470 MHz, DMSO-*d*₆, C₆F₆): δ -66.9 to -66.1 (m, 12.0F, CF₃), -62.6 (s, 6.0F, CF₃).

Polymer reaction of polymer 6 with tert-butyl bromoacetate

The NMP solution (3 mL) containing polymer **6** (137.8 mg, 3.0 mmol), Cs₂CO₃ (488.7 mg, 1.5 mmol), and TBAB (4.6 mg, 5 mol%) was heated at 100 °C for 48 h under stirring. Then the reaction mixture was poured into citric acid aqueous solution. Resulting polymer was reprecipitated from THF into *n*-hexane and dried *in vacuo*. The yield of polymer was 133.0 mg. The degree of etherification of hydroxyl groups was 60%. IR (film, cm⁻¹): 3504 (ν O-H), 2979, 2884 (ν C-H), 1751 (ν C=O), 1613, 1517 (ν C=C, aromatic), 1371, 1002 (ν C-O-C, ester), 1328, 1048 (ν C-O-C, ether), 1255, 1208, 1173, 1140 (ν C-F). ¹H NMR (500 MHz, DMSO-*d*₆, TMS):

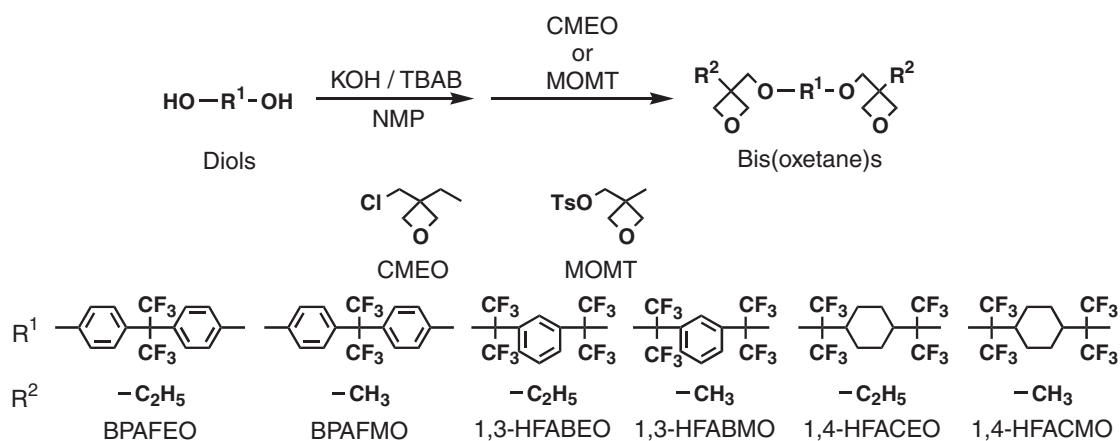
δ 0.82–1.94 (m, 26.8H, CH₃, CH₂, CH in cyclohexane), 3.35–4.68 (m, 14.4H, C–CH₂–O), 4.74 (brs, 0.8H, OH), 6.82–7.20 (m, 8.0H, aromatic H).

RESULTS AND DISCUSSION

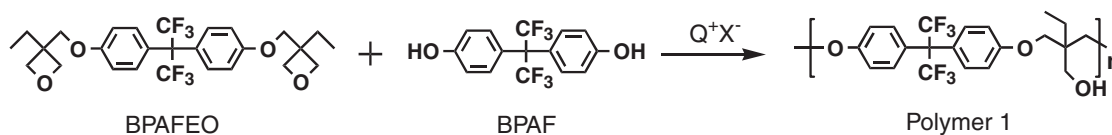
Fluorine-containing bis(oxetane)s were prepared by the reaction of fluorine-containing diols (BPAF, 1,3-HFAB and 1,4-HFAC) with CMEO and MOMT, respectively, using KOH (Scheme 1). The yields of BPAFEO, BPAFMO, 1,3-HFABEO, 1,3-HFABMO, 1,4-HFACEO, and 1,4-HFACMO were 93, 85, 89, 89, 69, and 63 %, respectively.

The polyaddition of the obtained fluorine-containing bis(oxetane) BPAFEO with BPAF was performed with certain catalysts or without any catalysts in bulk

at 180 °C for 48 h (Scheme 2), and the results are summarized in Table I. Polymer **1** was not obtained at all, when the reaction was carried out without a catalyst. On the other hand, polymer **1**s with low molecular weights were recovered in low yields using quaternary onium salts or crown ether complexes as catalysts. That is, polymer **1**s with $M_n = 2900$, $= 3400$, and $= 3400$ were obtained 20, 26, and 26 %, respectively, when the polyadditions were carried out with such catalysts as TPPC, TPPI, and 18-C-6/KCl. However, catalytic activities of TPPB, 18-C-6/KBr were relatively low. When the reaction was carried out using 18-C-6/KI, insoluble parts in THF were produced in 67 % yields. It seems that gel products were produced by the addition reaction of the produced primary hydroxyl groups in the side chain with oxetane rings at



Scheme 1.



Scheme 2.

Table I. Effect of catalyst on the polyaddition of BPAFEO with BPAF^a

No.	Catalyst	Yield ^b /%	$M_n \times 10^{-4c}$	M_w/M_n^c
1	None	0	—	—
2	TPPC	20	0.29	1.49
3	TPPB	12	0.30	1.45
4	TPPI	26	0.34	1.89
5	18-C-6/KCl	26	0.34	1.88
6	18-C-6/KBr	3	0.29	1.51
7	18-C-6/KI	2 (67) ^d	0.29	1.50
8	DBU	33	0.25	1.35
9	DMAP	20	0.22	1.32
10	<i>N</i> -Methyl imidazole	24	0.23	1.36

^aThe reaction was carried out with BPAFEO (0.5 mmol) and BPAF (0.5 mmol) using 5 mol% of catalysts in bulk at 180 °C for 48 h. ^bInsoluble parts in mixed solvents of Et₂O and *n*-hexane [1:5, v/v]. ^cEstimated by GPC (DMF) based on polystyrene standards. ^dInsoluble parts in THF.

Table II. Effect of co-catalysts on the polyaddition of BPAFEO with BPAF^a

No.	Catalyst (mol%/mol%)	Yield ^b /%	$M_n \times 10^{-4}$ ^c	M_w/M_n ^c
1	DBU/TPPC (2.5/2.5)	36	0.20	1.36
2	DMAP/TPPC (2.5/2.5)	27	0.20	1.36
3	DBU/TPPC (5.0/5.0)	57	0.31	1.34
4	DMAP/TPPC (5.0/5.0)	42	0.29	1.45

^aThe reaction was carried out with BPAFEO (0.5 mmol) and BPAF (0.5 mmol) using various catalysts in bulk at 180 °C for 48 h. ^bInsoluble parts in mixed solvents of Et₂O and *n*-hexane [1:5, v/v]. ^cEstimated by GPC (DMF) based on polystyrene standards.

the end of the polymer chain because catalytic activity of 18-C-6/KI was relatively high. Furthermore, it was found that the polymer was also obtained with certain organic bases such as DBU, DMAP, and *N*-methylimidazol. This means that the reaction proceeded by the addition of organic bases, because these organic bases were accelerate to deprotonate the phenolic proton of BPAF. The structure of polymer **1** was confirmed by IR, ¹H NMR and ¹⁹F NMR spectra.

Based on the above results, the effect of co-catalysts composed from quaternary onium salts and organic bases was investigated on the polyaddition reaction of BPAFEO with BPAF. The results are summarized in Table II. The yield of resulting polymer (polymer **1**) increased using the co-catalysts composed from quaternary onium salts and organic bases; however, the M_n 's of the polymer were nearly equal to that of the resulting polymer using quaternary onium salts or organic bases as catalysts. This means that the mixture of TPPC and DBU as co-catalysts had higher catalytic activity than the mixture of TPPC and DMAP on the polyaddition of BPAFEO with BPAF, because DBU was strong base than DMAP.

The effect of the reaction temperature on the polyaddition of BPAFEO with BPAF was examined using TPPC and DBU as the co-catalyst without solvent for 48 h. As shown in Figure 1, although the reaction of

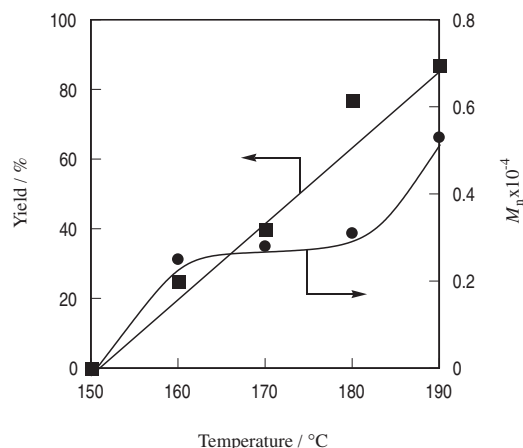


Figure 1. Effect of reaction temperature on the polyaddition of BPAFEO (0.5 mmol) with BPAF (0.5 mmol) using TPPC/DBU (5 mol%/5 mol%) in bulk for 48 h.: (●) M_n ; (■) yield.

BPAFEO with BPAF did not proceed at 150 °C, the yields of polymer **1** increased linearly with reaction temperature from 160 to 190 °C. On the other hand, The M_n 's of polymer **1** were not high, even though when the polyaddition was carried out at 160–180 °C. However, the M_n of polymer **1** increased remarkably at 190 °C, and the polymer with $M_n = 5300$ was obtained.

The effect of reaction time on the polyaddition of BPAFEO with BPAF was investigated using TPPC and DBU without solvent at 190 °C. As shown in Figure 2, the yield of resulting polymer increased gradually for 48 h. On the other hand, the M_n 's of the polymer gradually increased even beyond 120 h. This shows that the reaction proceed gradually by the typical step-growth reaction.

According to the obtained information on the polyaddition of BPAFEO with BPAF, polyadditions of certain bis(oxetane)s such as BPAFMO, 1,3-HFA-BEO, 1,3-HFABMO, 1,4-HFACEO, and 1,4-HFACMO with BPAF were examined using TPPC/DBU (5 mol%/5 mol%) as the co-catalyst in bulk at 190 °C at 72 h or 120 h (Scheme 3). The reaction conditions and results are summarized in Table III.

As summarized in Table III, the polyaddition of various bis(oxetane)s with BPAF proceeded, corresponding polymers **2**, **4**, and **6** were obtained in good yields by the polyaddition of bis(oxetane)s with meth-

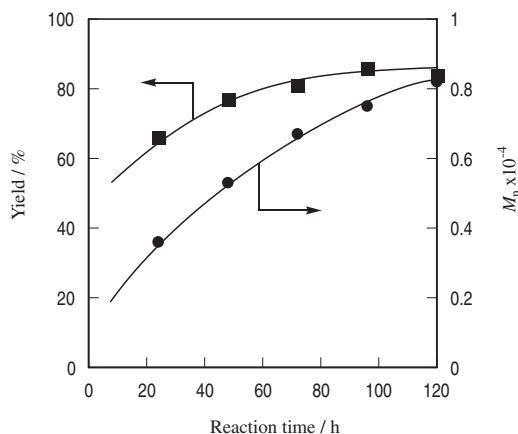
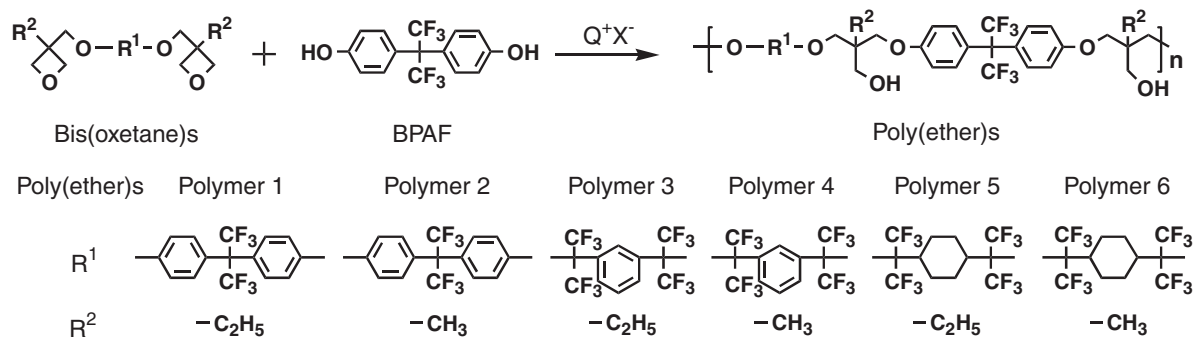


Figure 2. Effect of reaction time on the polyaddition of BPAFEO (0.5 mmol) with BPAF (0.5 mmol) using TPPC/DBU (5 mol%/5 mol%) in bulk at 190 °C: (●) M_n ; (■) yield.



Scheme 3.

Table III. Synthesis of certain poly(ether)s by the polyaddition of bis(oxetane)s with BPAF^a

Poly(ether)s	Bis(oxetane)s	Time/h	Yield ^b /%	$M_n \times 10^{-4c}$	M_w/M_n^c
Polymer 1	BPAFEO	120	84	0.82	2.61
Polymer 2	BPAFMO	72	93	0.91	4.67
Polymer 3	1,3-HFABEO	120	40	1.07	1.80
Polymer 4	1,3-HFABMO	72	77	1.05	2.09
Polymer 5	1,4-HFACEO	120	40	1.08	1.89
Polymer 6	1,4-HFACMO	72	83	1.07	2.85

^aThe reaction was carried out with bis(oxetane)s (0.5 mmol) and BPAF (0.5 mmol) using TPPC/DBU (5 mol%/5 mol%) without solvent at 190 °C. ^bInsoluble parts in mixed solvents of Et₂O and *n*-hexane (1:5, v/v). ^cEstimated by GPC (DMF) based on polystyrene standards.

yl group on the oxetane moiety such as BPAFMO, 1,3-HFABMO, and 1,4-HFACMO with BPAF at 72 h; however, soluble polymers were not obtained at 120 h. That is, insoluble gel products were obtained by the side reaction such as addition reaction of the produced pendant primary hydroxyl groups in the polymer with oxetane rings at the end of the polymer chain at 120 h. In addition, the yields of polymer 1, 3, and 5 were lower than those of 2, 4, and 6. This may be attributed to steric hindrance of the ethyl group higher than that of the methyl group on the oxetane moiety. This means that the reactivity of bis(oxetane)s on the polyaddition was strongly affected by the substituent groups on the oxetane moiety. The structures of all resulting polymers were confirmed by IR, ¹H NMR, and ¹⁹F NMR spectra.

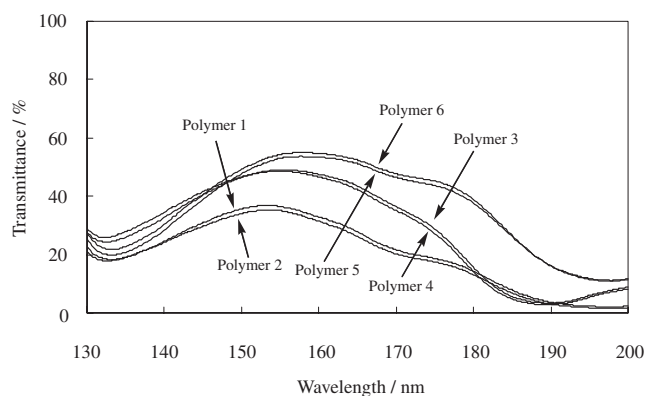
T_g 's of the resulting polymers were measured by DSC (Table IV). The T_g 's of resulting polymers containing BPAF structure were exhibited above 80 °C. The T_g 's of polymers 1, 2 with BPAF skeleton were 108, 107 °C, respectively which were relatively high T_g . Polymers 3–6 with flexible unit such as 1,3-HFAB or 1,4-HFAC were observed in the range of 84–90 °C. This result means that the thermal properties of fluoropolymers increased in following order of their monomers, BPAF > 1,3-HFAB \approx 1,4-HFAC.

The transmittance at 157 nm and VUV spectra of resulting polymers were measured by VUV spectrometer (Table IV and Figure 3). Relationship between transmittance at 157 nm and the fluorine contents of

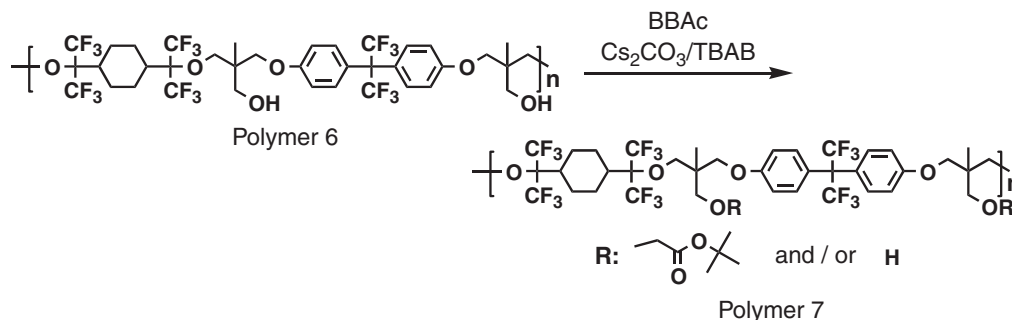
Table IV. Characteristics of the poly(ether)s

Poly(ether)s	T_g^a /°C	T_d^b /°C	T^c at 157 nm/%
Polymer 1	108	435	35
Polymer 2	107	444	34
Polymer 3	84	440	49
Polymer 4	85	444	48
Polymer 5	85	433	54
Polymer 6	90	441	55

^aDetermined by DSC at heating rate of 10 °C/min in nitrogen. ^bDetermined by TG/DTA at heating rate of 10 °C/min in nitrogen. ^cFilm thickness: 1000 Å

**Figure 3.** VUV spectra of poly(ether)s (film thickness: 1000 Å).

these polymers are shown in Figure 4. As a result, transmittance of polymer linearly increased with fluorine content of polymer. In addition, it seems that



Scheme 4.

Table V. Solubility of fluorine-containing poly(ether)s^a

Solvent	Polymer 1	Polymer 2	Polymer 3	Polymer 4	Polymer 5	Polymer 6
<i>n</i> -Hexane	–	–	–	–	–	–
Methanol	++	++	++	++	++	++
Acetonitrile	+	+	++	++	++	++
Acetone	++	++	++	++	++	++
Ethyl acetate	++	++	++	++	++	++
Chloroform	++	++	++	++	++	++
Toluene	++	++	++	++	++	++
Anisole	++	++	++	++	++	++
<i>o</i> -Dichlorobenzene	++	++	++	++	++	++
THF	++	++	++	++	++	++
DMF	++	++	++	++	++	++
NMP	++	++	++	++	++	++
DMSO	++	++	++	++	++	++

^a ++: soluble at room temperature, +: soluble by heating, –: insoluble

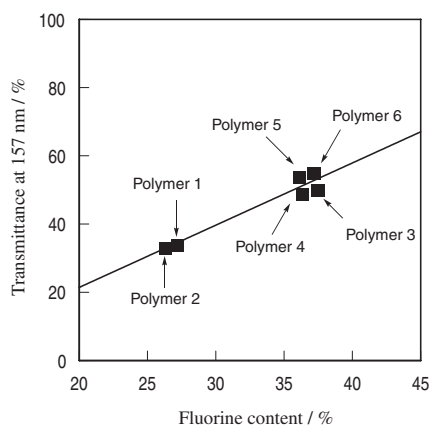


Figure 4. Relationship between transmittance at 157 nm for 0.1 mm thickness and fluorine content (%) of the poly(ether)s.

transparency of aliphatic ring such as 1,4-HFAC is higher than that of aromatic ring such as 1,3-HFAB. These results show that thus obtained poly(ether)s are highly transparent at 157 nm for 0.1 μm thickness.

The solubility of the resulting polymers was examined. As summarized in Table V, all of the obtained polymers were soluble in all solvents except *n*-hexane. It was found that the obtained fluoropolymers had good solubility.

To estimate the usefulness of poly(ether)s with

pendant primary hydroxyl groups as reactive polymers, the chemical modification of polymer 6 was investigated. The reaction of polymer 6 with 3.0 equiv of BBAC was carried out using Cs_2CO_3 and TBAB in NMP at 100 °C for 48 h, and polymer 7 with pendant *tert*-butyl ester moieties was obtained. The degree of etherification of hydroxyl groups of the polymer was 60%, which was evaluated by $^1\text{H NMR}$. The structure of polymer 7 was confirmed by IR and $^1\text{H NMR}$ spectra. From these results, polymer 7 with pendant *tert*-butyl ester moieties could be used as positive resists.

CONCLUSION

Fluorine-containing bis(oxetane)s were obtained by the reaction of fluorine-containing diols with oxetane compounds in good yields. The polyaddition of bis(oxetane)s with BPAF proceeds to produce corresponding soluble polymer with high molecular weight under appropriate conditions. Resulting polymers are highly transparent at 157 nm. Furthermore, primary hydroxyl groups of obtained poly(ether)s are useful as a reactive groups, and poly(ether)s with pendant *tert*-butyl ester moieties were obtained by the polymer reaction.

Acknowledgment. The authors would like to thank Dr. T. Shimokawa and H. Iwasawa of JSR Corporation for VUV measurement.

REFERENCES

1. C. G. Willson, B. C. Trinqué, B. P. Osborn, C. R. Chambers, Y. Hsieh, T. Chiba, P. Zimmerman, D. Miller, and W. Conley, *J. Photopolym. Sci. Technol.*, **15**, 583 (2002).
2. a) Y. C. Bae, K. Douki, T. Yu, J. Dai, D. Schmaljohann, S. H. Kang, K. H. Kim, H. Koerner, W. Conley, D. Miller, R. Balasubramanian, S. Holl, and C. K. Ober, *J. Photopolym. Sci. Technol.*, **14**, 613 (2001).
b) C. K. Ober, K. Douki, V. R. Vohra, Y. Kwark, X. Liu, W. Conley, D. Miller, and P. Zimmerman, *J. Photopolym. Sci. Technol.*, **15**, 603 (2002).
3. W. Conley, D. Miller, C. Chambers, B. C. Trinqué, B. Osborn, T. Chiba, P. Zimmerman, R. Dammel, A. Romano, and C. G. Willson, *J. Photopolym. Sci. Technol.*, **15**, 613 (2002).
4. a) M. Shirai, T. Shinozuka, H. Okamura, M. Tsunooka, S. Kishimura, M. Endo, and M. Sasago, *J. Photopolym. Sci. Technol.*, **14**, 621 (2001).
b) S. Kishimura, M. Endo, and M. Sasago, *J. Photopolym. Sci. Technol.*, **15**, 625 (2002).
5. T. Fujigaya, S. Ando, Y. Shibasaki, S. Kishimura, M. Endo, S. Sasago, and M. Ueda, *J. Photopolym. Sci. Technol.*, **15**, 643 (2002).
6. H. Ito, G. M. Wallraff, N. Fender, P. J. Brock, C. E. Larson, H. D. Truong, G. Breyta, D. C. Miller, M. H. Sherwood, and R. D. Allen, *J. Photopolym. Sci. Technol.*, **14**, 583 (2001).
7. N. Ito, S. Tonosaki, H. Kudo, A. Kameyama, and T. Nishikubo, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 1395 (2002).
8. N. Ito, H. Kudo, A. Kameyama, T. Nishikubo, and T. Anada, *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 213 (2003).
9. Y. Konno, H. Kudo, A. Kameyama, and T. Nishikubo, *J. Polym. Sci., Part A: Polym. Chem.*, in press.
10. T. Nishikubo, A. Kameyama, and A. Suzuki, *React. Funct. Polym.*, **37**, 19 (1998).
11. T. Nishikubo, A. Kameyama, M. Ito, and A. Suzuki, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 2873 (1998).
12. T. Nishikubo, A. Kameyama, M. Ito, T. Nakajima, and H. Miyazaki, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 2781 (1999).
13. T. Nishikubo, A. Kameyama, and K. Tsutsui, *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 1169 (2000).