Cationic Photopolymerization of Epoxides by Direct and Sensitized Photolysis of Onium Tetrakis(pentafluorophenyl)borate Initiators

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ABSTRACT: Cationic photopolymerization of epoxides by the direct and sensitized photolysis of eight onium tetrakis(pentafluorophenyl)borates as initiators has been investigated. The relative reactivity of the onium borates on the photopolymerization was studied by the measurement of spectral sensitivity and by real time Fourier transform infrared spectroscopy. The kinetics of the photopolymerization by the sensitized photolysis was different from that of the direct photolysis. Several onium borates were sensitized by the excited singlet state of the anthracenes (nonsubstituted anthracene and 9-methyl- and 9,10-dimethylanthracene), and the rates of polymerization increased with decreasing free energy changes between the onium borates and the excited singlet state of 9-methylanthracene. The acid generated by the photodecomposition of the onium borates produced nonacidic products by heating.

Introduction

There has been a growing interest in recent years in cationic photopolymerization due to the development of efficient cationic photoinitiators. Cationic polymerizable monomers such as epoxides are polymerized by cationic species such as acids. Several onium salts,[1] e.g., diaryliodonium salts,[2−15] triarylsulfonium salts,[6−20] and phenacylsulfonium salts,[21−24] serve as cationic photoinitiators. They are decomposed by absorbing light, generate acids, and initiate cationic polymerization of epoxides (Scheme 1). Since most of these onium salts significantly absorb light only below ca. 300 nm, technologically useful spectral response requires that photolysis of the onium salts are spectrally sensitized. For this reason, the sensitized photolysis[5−14,16,17] as well as the direct photolysis[2−5,14,15,17−20,22−24] of the onium salts has been investigated.

Recently, it was reported that diphenyliodonium tetrakis(pentafluorophenyl)borate (**IFB**) serves as a more efficient cationic photoinitiator for the epoxy silicons than the corresponding diphenyliodonium salts containing an inorganic anion such as BF_4^-, PF_6^-, and SbF_6^-.[25,26] Nevertheless **IFB** hardly absorbs light above 300 nm, and sensitized polymerization using **IFB** with sensitizers had never been examined.

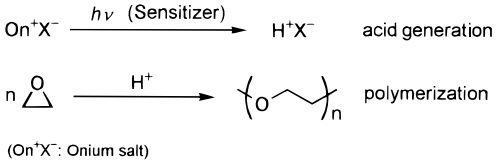
In a previous paper, we reported that **IFB** is sensitized by several anthracenes and initiates photopolymerization of an epoxide.[27] In this paper, we report cationic photopolymerization of epoxides by the direct and sensitized photolysis of new onium tetrakis(pentafluorophenyl)borates as well as **IFB**. The reactivity of eight onium tetrakis(pentafluorophenyl)borates as cationic initiators is compared, since only few attempts have been made so far to investigate the effect of the different cation of various onium salts on cationic photopolymerization.

Experimental Section

IR spectra were recorded on a Jasco FT/IR-300E Fourier transform infrared spectrometer except real time Fourier transform infrared (RT−FTIR) spectroscopy.[31−34] ^{1}H and ^{13}C NMR spectra were measured using a JEOL GSX400 NMR spectrometer (400 and 100 MHz, respectively). Chemical shifts are in ppm with tetramethylsilane as the internal standard. The molecular weight of a prepared copolymer was measured on a Tosoh SC-8020 gel permeation chromatography (GPC) with a TSKgel G2000XL column (Tosoh) in tetrahydrofuran as an eluent. Absorption and fluorescence spectra were recorded on a Jasco V-530 UV/vis spectrophotometer and a Jasco FP-770F spectrofluorometer, respectively. Fluorescence decays were measured by a time-corrected single photon counting apparatus (Horiba, NAES-550) equipped with a nitrogen lamp; the emissions were monitored through a cutoff filter (Hoya, L-42) to minimize the scattering. Reduction potentials (E_{red}) of the onium borates were measured by cyclic voltammetry on a CV-50W voltammetric analyzer (BAS Inc.) with a scan rate of 100 mV/s in dry acetonitrile under argon at room temperature. A platinum-inlay electrode was used as a working electrode along with a platinum auxiliary electrode and an $Ag/AgClO_4$ reference electrode. The electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile. An electrode was calibrated with ferrocene using its known reduction value (0.06 V vs Ag/Ag^+)[28] and converted to that relative to SCE by the addition of 0.337 V. The E_{red} values of the onium borates except 4-cyano-1-phenacylpyridinium tetrakis(pentafluorophenyl)borate (**PyFB2**) stand for peak potentials (E_{peak}). The E_{red} value of **PyFB2** stands for redox potential ($E_{1/2}$).

Cyclohexanone, toluene (reagent grade), dichlorometane (spectrophotometric grade), and hexane (HPLC analytical grade) were used as received from Kanto Chemical Co., Inc. Anthracene (**An**), 9-methylanthracene (**MAn**), 9,10-dimethylanthracene (**DMAn**), *N*-phenacylpyridinium bromide, azobis(isobutyronitrile), and pentafluorobenzene were obtained from Tokyo Chemical Industries Co., Ltd. Methyl methacrylate (MMA, Kanto Chemical Co., Inc.), 3,4-epoxycyclohexylmethyl methacrylate (Cyclomer M100, Daicer Chemical Ind. Co. Ltd.), 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL-4221, Union Carbide Chemical and Plastics Co. Inc.), poly(methyl methacrylate) (PMMA, M_w = 996 000, Aldrich

Scheme 1



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Chemical Co., Inc.), lithium tetrakis(pentafluorophenyl)borate (Tosoh Akzo Co.), dimethyl-4-hydroxyphenylsulfonium methyl sulfate (Wako Pure Chemical Ind., Ltd.), and dimethyl-4-acetoxyphenylsulfonium methyl sulfate (Wako Pure Chemical Ind., Ltd.) were purchased. Dimethylphenacylsulfonium bromide,[22] benzyl(4-hydroxyphenyl)methylsulfonium chloride,[29] 4-cyano-1-phenacylpyridinium bromide,[30] diphenyliodonium tetrakis(pentafluorophenyl)borate (**IFB**),[25] and dimethylphenacylsulfonium tetrakis(pentafluorophenyl)borate (**SFB1**)[27] were prepared according to the reported procedure. The preparations of onium tetrakis(pentafluorophenyl)borates and the copolymer poly(MMA-*co*-M100) are carried out as follows.

General Procedure for Preparation of Onium Tetrakis(pentafluorophenyl)borates. A 20 mmol sample of onium halide was dissolved in 100 mL of water in a 300 mL Erlenmeyer flask. Then 20 mmol of lithium tetrakis(pentafluorophenyl)borate dissolved in 100 mL of water was added dropwise. The mixture was stirred for 30 min and then filtered. The residual product was washed with water and then dried in the dark overnight in vacuo. Onium tetrakis(pentafluorophenyl)borate was obtained.

Dimethylbenzylsulfonium Tetrakis(pentafluorophenyl)borate (SFB2). Compound **SFB2** was obtained from dimethylbenzylsulfonium bromide in 79% yield as a white powder: mp 178−180 °C dec; ^{1}H NMR (DMSO-d_6) δ 2.85 (s, 6H, (CH_3)$_2$S$^+$), 4.71 (s, 2H, C$_6$H$_5$CH_2), 7.51 (sm, 5H, C$_6$$H_5$); ^{13}C NMR (DMSO-$d_6$) δ 23.98 (s, (CH_3)$_2S^+$), 45.94 (C$_6H_5$CH_2), 123.5 (sm, $C_6F_5B^-$), 128.24 (s, C_6H_5), 129.25 (s, C_6H_5), 129.54 (s, C_6H_5), 130.63 (s, C_6H_5), 135.58 (dm, J_{C-F} = 238 Hz, $C_6F_5B^-$), 137.62 (dm, J_{C-F} = 246 Hz, $C_6F_5B^-$), 147.52 (dm, J_{C-F} = 240 Hz, $C_6F_5B^-$); IR (KBr) 1645, 1516, 1464, 1275, 1084, 980, 773, 756, 685, 661 cm^{-1}. Anal. Calcd for $C_{33}H_{13}BF_{20}OS$: C, 47.62; H, 1.574. Found: C, 47.68; H, 1.59.

Dimethyl-4-hydroxyphenylsulfonium Tetrakis(pentafluorophenyl)borate (SFB3). Compound **SFB3** was obtained from dimethyl-4-hydroxyphenylsulfonium methyl sulfate in 74% yield as a white powder: mp 189−191 °C dec; ^{1}H NMR (DMSO-d_6) δ 3.26 (s, 6H, (CH_3)$_2$S$^+$), 3.65 (s, broad, 1H, OH), 7.10 (d, 2H, J = 8.8 Hz, C_6H_4), 7.95 (d, 2H, J = 8.8 Hz, C_6H_4); ^{13}C NMR (DMSO-d_6) δ 29.14 (s, (CH_3)$_2$S$^+$), 113,91 (s, HOC_6H_4), 117.33 (s, HOC_6H_4), 123.5 (sm, $C_6F_5B^-$), 132.19 (s, HOC_6H_4), 135.66 (dm, J_{C-F} = 240 Hz, $C_6F_5B^-$), 137.71 (dm, J_{C-F} = 246 Hz, $C_6F_5B^-$), 147.59 (dm, J_{C-F} = 237 Hz, $C_6F_5B^-$), 162.57 (s, HOC_6H_4); IR (KBr) 3586, 1645, 1587, 1516, 1462, 1277, 1211, 1090, 980, 775, 756, 685, 661 cm^{-1}. Anal. Calcd for $C_{32}H_{11}BF_{20}OS\cdot H_2O$: C, 45.09; H, 1.537. Found: C, 44.82; H, 1.54.

Dimethyl-4-acetoxyphenylsulfonium Tetrakis(pentafluorophenyl)borate (SFB4). Compound **SFB4** was obtained from dimethyl-4-acetoxyphenylsulfonium methyl sulfate in 73% yield as a white powder: mp 153−155 °C dec; ^{1}H NMR (DMSO-d_6) δ 2.35 (s, 3H, CH_3O), 3.34 (s, 6H, (CH_3)$_2$S$^+$), 7.56 (d, 2H, J = 8.8 Hz, C_6H_4), 8.20 (d, 2H, J = 8.8 Hz, C_6H_4); ^{13}C NMR (DMSO-d_6) δ 20.88 (s, CH$_3$CO), 28.62 (s, (CH_3)$_2$S$^+$), 123.5 (sm, $C_6F_5B^-$), 123.66 (s, C_6H_4), 124.08 (s, C_6H_4), 131.72 (s, C_6H_4), 135.65 (dm, J_{C-F} = 248 Hz, $C_6F_5B^-$), 137.67 (dm, J_{C-F} = 245 Hz, $C_6F_5B^-$), 147.53 (dm, J_{C-F} = 239 Hz, $C_6F_5B^-$), 154.37 (s, C_6H_4), 168.67 (s, C=O); IR (KBr) 3037, 1761 (C=O), 1645, 1516, 1462, 1373, 1275, 1203, 1173, 1088, 980, 775, 756, 685, 661 cm^{-1}. Anal. Calcd for $C_{34}H_{13}BF_{20}OS$: C, 46.60; H, 1.495. Found: C, 46.66; H, 1.53.

Benzyl(4-hydroxyphenyl)methylsulfonium Tetrakis(pentafluorophenyl)borate (SFB5). Compound **SFB5** was obtained from benzyl(4-hydroxyphenyl)methylsulfonium chloride[29] in 77% yield as a white powder: mp 56−58 °C dec; ^{1}H NMR (DMSO-d_6) δ 3.25 (s, 2H, C$_6$H$_5$CH_2), 4.90 (d, 1H, J = 12.4 Hz, C$_6$H$_5$CH_2), 5.07 (d, 1H, J = 12.4 Hz, C$_6$H$_5$CH_2), 7.45−7.51 (m, 5H, C$_6$$H_5$), 7.04 (d, 2H, J = 8.8 Hz, C_6H_4), 7.22−7.30 (m, 2H, C$_6$$H_5$), 7.35−7.42 (m, 3H, C$_6$$H_5$), 7.77 (d, 2H, J = 8.8 Hz, C_6H_4), 10.87 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 26.11 (s, CH$_3$S$^+$), 50.42 (CH$_2$C$_6$H$_5$), 110.64 (s, HOC_6H_4), 117.31 (s, HOC_6H_4), 123.5 (sm, $C_6F_5B^-$), 128.42 (s, CH$_2$C$_6$H$_5$), 128.99 (s, CH$_2$C$_6$H$_5$), 129.45 (s, CH$_2$C$_6$H$_5$), 130.41 (s, CH$_2$C$_6$H$_5$), 133.16 (s, HOC_6H_4), 135.60 (dm, J_{C-F} = 247 Hz, $C_6F_5B^-$), 137.63 (dm, J_{C-F} = 245 Hz, $C_6F_5B^-$), 147.49 (dm, J_{C-F} = 241 Hz, $C_6F_5B^-$), 162.70 (s, HOC_6H_4); IR (KBr) 3586, 1645, 1585, 1516, 1464, 1277, 1088, 980, 773, 756, 685, 661 cm^{-1}. Anal. Calcd for $C_{38}H_{15}BF_{20}OS$: C, 50.13; H, 1.660. Found: C, 50.13; H, 1.71.

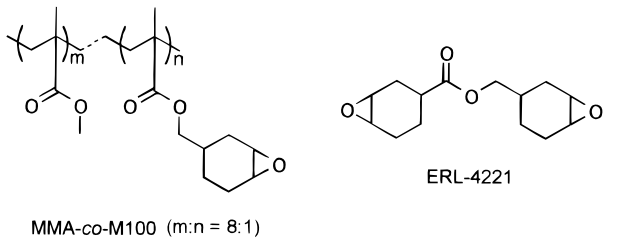


Figure 1. Structures of the epoxides used.

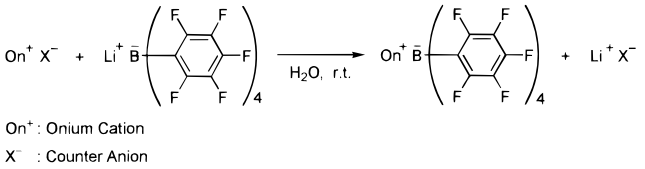
***N*-Phenacylpyridinium Tetrakis(pentafluorophenyl)borate (PyFB1).** Compound **PyFB1** was obtained from *N*-phenacylpyridinium bromide in 76% yield as a white powder: mp 188−190 °C dec; ^{1}H NMR (DMSO-d_6) δ 6.46 (s, 2H, COCH_2), 7.60−7.69 (m, 2H, *m*-C$_6$$H_5$CO), 7.75−7.82 (m, 1H, *p*-C$_6$$H_5$CO), 8.00−8.08 (m, 2H, *o*-C$_6$$H_5$CO), 8.25−8.30 (m, 2H, 3-N$^+$C$_5$$H_5$); 8.70−8.80 (m, 2H, 4-N$^+C_5$$H_5$); 8.95−9.05 (m, 2H, 2-N$^+C_5$$H_5$); ^{13}C NMR (DMSO-$d_6$) δ 66.24 (s, COCH_2), 123.5 (sm, $C_6F_5B^-$), 127.87 (s, N$^+$$C_5H_5$), 128.23 (s, *o*-$C_6H_5$CO), 129.13 (s, *m*-$C_6H_5$CO), 133.52 (s, *ipso*-$C_6H_5$CO), 134.73 (s, *p*-$C_6H_5$CO), 136.07 (dm, J_{C-F} = 238 Hz, $C_6F_5B^-$), 137.52 (dm, J_{C-F} = 246 Hz, $C_6F_5B^-$), 146.30 (s, N$^+$$C_5H_5$), 147.40 (dm, J_{C-F} = 240 Hz, $C_6F_5B^-$), 148.68 (s, N$^+$$C_5H_5$), 190.63 (s, C=O); IR (KBr) 1711 (C=O), 1639, 1516, 1462, 1277, 1084, 980, 776, 685 cm^{-1}. Anal. Calcd for $C_{37}H_{12}BF_{20}NOS$: C, 50.65; H, 1.378; N, 1.596. Found: C, 50.68; H, 1.38; N, 1.68.

4-Cyano-1-phenacylpyridinium Tetrakis(pentafluorophenyl)borate (PyFB2). Compound **PyFB2** was obtained from 4-cyano-1-phenacylpyridinium bromide[30] in 76% yield as pale purplish white powder: mp 94−96 °C dec; ^{1}H NMR (DMSO-d_6) δ 6.53 (s, 2H, COCH_2), 7.60−7.69 (m, 2H, *m*-C$_6$$H_5$-CO), 7.75−7.82 (m, 1H, *p*-C$_6$$H_5$CO), 8.00−8.08 (m, 2H, *o*-C$_6$$H_5$-CO), 8.81 (d, 2H, J = 7.2 Hz, N$^+$C$_5$$H_4$CN), 9.25 (d, 2H, J = 7.2 Hz, N$^+$C$_5$$H_4$CN); ^{13}C NMR (DMSO-$d_6$) δ 67.12 (s, COCH_2), 114.83 (*C*N), 123.5 (sm, $C_6F_5B^-$), 127.92 (s, N$^+$$C_5H_4$), 128.31 (s, *o*-$C_6H_5$CO), 129.19 (s, *m*-$C_6H_5$CO), 130.74, 133.32 (s, *ipso*-C_6H_5CO), 134.89 (s, *p*-C_6H_5CO), 136.07 (dm, J_{C-F} = 238 Hz, $C_6F_5B^-$), 137.52 (dm, J_{C-F} = 246 Hz, $C_6F_5B^-$), 147.40 (dm, J_{C-F} = 240 Hz, $C_6F_5B^-$), 147.67 (s, N$^+$$C_5H_4$), 189.81 (s, C=O); IR (KBr) 1703 (C=O), 1645, 1516, 1462, 1275, 1225, 1088, 978, 773, 756, 685, 661 cm^{-1}. Anal. Calcd for $C_{38}H_{15}BF_{20}NOS$: C, 50.58; H, 1.228; N, 3.104. Found: C, 50.53; H, 1.31; N, 3.15.

Preparation of Poly(MMA-*co*-M100). Copolymerization of MMA and 3,4-epoxycyclohexylmethyl methacrylate (M100) was carried out in a 1 L separable flask equipped with a condenser, a nitrogen gas inlet, and a mechanical stirrer. The mixture of MMA (80 g), M100 (20 g), cyclohexanone (600 g), and azobis(isobutyronitrile) (3.0 g) was charged to the flask and was purged with nitrogen gas. The mixture was heated with stirring at 80 °C for 6 h. After the reaction, the mixture containing the copolymer poly(MMA-*co*-M100) was used for the measurement of the sensitivity without purification. The copolymer was characterized by GPC: M_n = 10 500, M_w = 19 200; M_w/M_n = 1.82. The structures of the copolymer poly(MMA-*co*-M100) and an epoxide ERL-4221 are shown in Figure 1.

Measurements of Spectral Sensitivity. A sample solution was prepared by mixing the cyclohexanone solution (7 g) containing the poly(MMA-*co*-M100) (1 g), the onium borates as an initiator (6.5×10^{-5} mol), and the anthracenes as a sensitizer (6.5×10^{-5} mol). The photosensitive plate was prepared by coating the sample solution onto a glass plate by a spin coator (Mitsui Seiki Co., with 500 rpm for 5 s) and by drying it at 50 °C for 10 min in an oven. Thickness of the photopolymerizable film on the plate was measured by a surface profile measuring system (Veeco Instruments Inc., Dektak 3030) and was found to be ca. 10 μm. The plate was placed into a spectral irradiator (Jasco, MSS-25 spectral irradiator) equipped with a 500 W xenon lamp (Ushio Inc., UXL-500D) and was irradiated with varying exposure time

Scheme 2



On$^+$: Onium Cation

X$^-$: Counter Anion

with monochromatic light by grating the light from the lamp. Incident angle of the light was 90° onto the plate. The irradiated plate was developed in tap toluene at 20 °C. The energy of the light required to cure the photopolymerizable film was defined as the sensitivity.

Real Time FTIR Study on Photopolymerization of an Epoxide. Kinetic study of photopolymerization of ERL-4221 was analyzed by real time Fourier transform infrared (RT−FTIR) spectroscopy.[31−34] A sample solution was prepared by mixing cyclohexanone (8 g), ERL-4221 (0.5 g), PMMA (0.5 g), the onium borates (6.5×10^{-5} mol), and the anthracenes (6.5×10^{-5} mol). A photosensitive plate was prepared by coating the sample solution onto a stainless steel plate (mesh no. 600). Thickness of a photopolymerizable film on the plate was found to be ca. 10 μm. The plate was placed into an IR spectrometer (Nicolet, Magna 560 FTIR spectrometer) equipped with a liquid nitrogen cooled MCT detector and attached with a grazing angle accessory (Graseby-Specac Co., 19650 series). The plate was irradiated with UV light from a high-pressure mercury lamp (Ushio Inc., UXM-200YA) while IR spectra of it were measured. IR spectra were recorded at the rate of 120 spectra/min with resolution of 4 cm^{-1} and were processed using OMNIC rapid scan software version 2.0 (Nicolet). Irradiation of the UV light was carried out by either without optical filters (in the case of the direct photolysis) or after passing through a band-pass filter to obtain 365 nm light (in the case of the sensitized photolysis). Incident angles of the UV light and an IR beam of the IR spectrometer to the plate were 90 and 60° onto the plate, respectively. Intensity of the UV light at the plate position was measured by an optical power meter (Ushio Inc., UTI-150 Unimeter) and was found to be either 800 W/m^2 (at 254 nm, the direct photolysis case) or 960 W/m^2 (at 365 nm, the sensitized photolysis case). All the RT−FTIR experiments were carried out under air atmosphere.

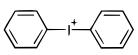
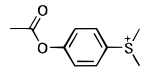
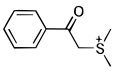
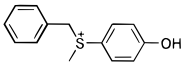
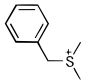
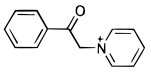
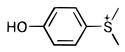
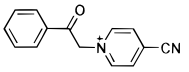
Analysis of Photoproducts. The photosensitive plate was prepared and irradiated in the same manner as the RT−FTIR experiment with a glass plate instead of a stainless steel plate. A 0.1 g sample of the irradiated film was extracted with 0.5 mL of hexane. The hexane extract was analyzed by GC/MS. GC/MS spectra were measured on a HP 5970 mass selective detector coupled with a HP 5890 series II GC with a DB-5 column (J & W Scientific, 30 m × 0.25 mm i.d. × 0.25μm film thickness).

Results and Discussion

Preparation of Onium Tetrakis(pentafluorophenyl)borates. The onium tetrakis(pentafluorophenyl)-borates were prepared by the reaction of the corresponding onium salt precursors with lithium tetrakis-(pentafluorophenyl)borate in water at room temperature as shown in Scheme 2. Yield of the reaction is listed in Table 1. All the obtained onium borates were kept stable at room temperature for over 3 months and were shielded from air and moisture. To effectively initiate photopolymerization, solubility of initiators is a significant problem. All the onium borates were essentially soluble in various organic solvents, e.g., aromatic hydrocarbons, ketones, esters, and alcohols. However, they were insoluble in aliphatic hydrocarbons.

Figure 2 and Figure 3 show the absorption spectra of the onium borates. The spectra of the onium borates consist of the major absorption bands depending on the onium cation and a very weak long tail extending out as far as 350 nm. It is reported that the absorption spectrum of **IFB** shows the same tail.[25] The tail is due to the tetrakis(pentafluorophenyl)borate anion, since the absorption spectrum of lithium tetrakis(pentafluorophenyl)borate showed the same tail. All the onium borates except **PyFB2** did not show strong absorption above 350 nm. Only **PyFB2** showed an absorption maximum at 574 nm. The absorption maximum would be based on a charge transfer (CT) absorption. Although a CT absorption of 4-cyano-1-phenacylpyridinium salts is not known, it is reported that 4-cyano-1-alkylpyridinium salts show a CT absorption.[44]

Table 1. Preparation of Onium Tetrakis(pentafluorophenyl)borates[a]

	cation part	yield (%)		cation part	yield (%)
IFB		93	**SFB4**		73
SFB1		83	**SFB5**		77
SFB2		79	**PyFB1**		76
SFB3		74	**PyFB2**		76

[a] Counteranion is tetrakis(pentafluorophenyl)borate.

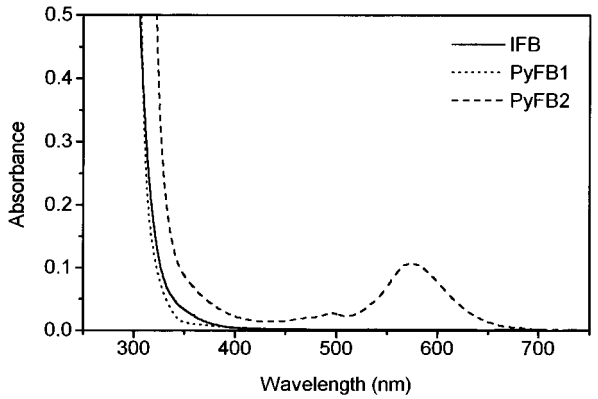


Figure 2. Absorption spectra of 1.0×10^{-3} M solutions of iodonium and pyridinium tetrakis(pentafluorophenyl)borates in dichloromethane.

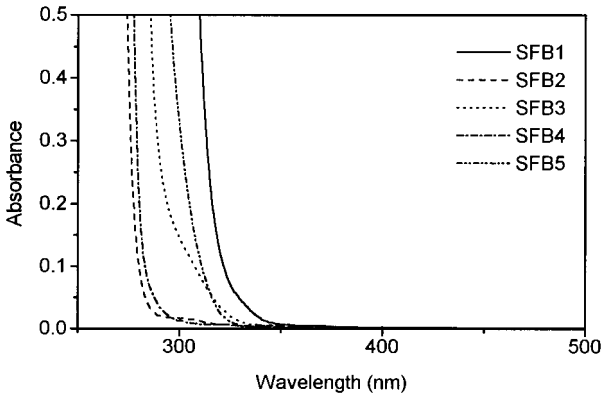


Figure 3. Absorption spectra of 1.0×10^{-3} M solutions of sulfonium tetrakis(pentafluorophenyl)borates in dichloromethane.

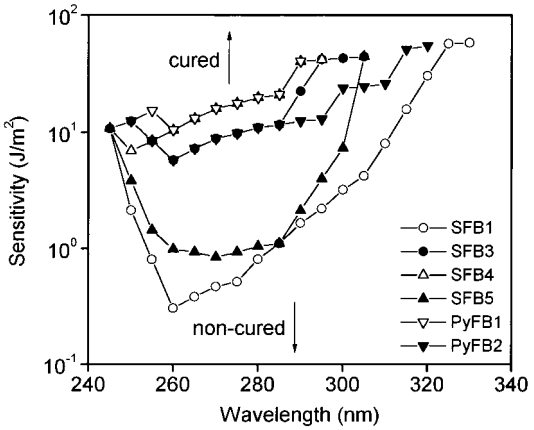


Figure 4. Spectral sensitivity of the poly(MMA-*co*-M100) film containing 7.7×10^{-2} M of the onium tetrakis(pentafluorophenyl)borates. Film thickness = 10 μm. Exposed to the light from a xenon lamp.

Photopolymerization by Direct Photolysis of Onium Tetrakis(pentafluorophenyl)borates. The relative reactivity of the onium borates was studied by the measurement of the spectral sensitivity and by RT−FTIR. Figure 4 shows the spectral sensitivity of the photopolymerizable film of the poly(MMA-*co*-M100) containing the onium borates. In the 260−280 nm region, both photopolymerizable films containing **SFB1** and **SFB5** showed high sensitivity. It is reported that the corresponding sulfonium salts, phenacylsulfonium[22] and benzyl(*p*-hydroxyphenyl)methylsulfonium[35−38] salts, serve as cationic photoinitiators. The sensitivities for **SFB3**, **SFB4**, **PyFB1**, and **PyFB2** were about 10 times lower than for **SBF1**. However, it is interesting that both **PyFB1** and **PyFB2** serve as cationic photoinitiators, since no studies have ever tried to apply *N*-phenacylpyridinium compounds as cationic photoinitiators. It is evident that the photopolymerizable film containing these onium borates were not sensitive to light with wavelength above 320 nm.

To obtain the kinetics profile of the photopolymerization, the cationic polymerization of a typical difunctional cycloaliphatic epoxide ERL-4221 in a PMMA film was investigated by RT−FTIR spectroscopy.[33,34] By simultaneous irradiation the photopolymerizable film containing the epoxide with UV light and recording its IR spectrum, the changes in the IR absorption bands of the epoxide undergoing photopolymerization can be monitored as a function of time. The epoxide shows an absorption band at 790 cm^{-1} corresponding to the C−H bond stretching vibration of an epoxy group.[33,39,40] Hence the progress of the photopolymerization can be followed by the decrease of the absorption band. Also of interest is the increase of the peaks at 3500 and 1080 cm^{-1} that correspond to the absorption of the hydroxy group (OH) and of the ether group (C−O−C) respectively in the poly(ether) formed during photopolymerization. Degree of conversion of the epoxide at any time during the UV irradiation can be obtained by measuring the peak height under the specific absorption band according to eq 1, where A_0 and A_t are the absorbance levels at 790

$$\text{degree of conversion} = \frac{A_0 - A_t}{A_0} \times 100\ (\%) \qquad (1)$$

cm^{-1} based on an epoxy group in the photopolymerizable film before and after UV irradiation during time t,

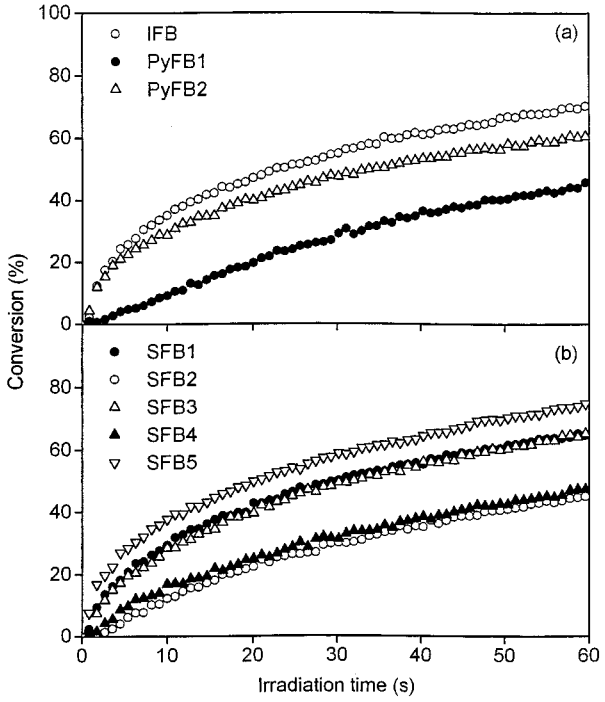


Figure 5. Photopolymerization profiles of an epoxide (ERL-4221) by direct photolysis of the onium tetrakis(pentafluorophenyl)borates in a PMMA film recorded by RT−FTIR spectroscopy exposed to the light of a high-pressure mercury lamp. [initiator] = 7.7×10^{-2} M in the mixture of ERL-4221 and PMMA (w/w = 1/1). Light intensity = 800 W/m^2 (254 nm).

respectively. From the kinetic curves, one can evaluate how many epoxy groups have polymerized, and thus determine both the actual rate of polymerization (R_p) at a given time:

$$R_p = [M]_0 \frac{A_{t1} - A_{t2}}{A_0(t_2 - t_1)} \qquad (2)$$

Here $[M]_0$ (=4.7 M) is the concentration of the epoxide in the film before irradiation, and t_1 and t_2 are the times between which the conversion data are collected. A plot of percent conversion vs irradiation time provides a kinetic curve for the photopolymerization. The slope of the initial linear portion of the curve corresponds to the factor $R_p/[M]_0$. This value gives a measure of the relative rates of photopolymerization of the epoxide. Irradiation was carried out using a high-pressure mercury lamp without optical filters in direct photolysis experiments. Since the onium borates, except **PyFB2**, in the photopolymerizable film absorbed less than 3% of the light at 365 nm, the direct photolysis of the onium borates would take place mainly by the light at 254 nm from the lamp.

Figure 5 shows the polymerization profiles of the epoxide in a PMMA film for comparing the onium borates by RT−FTIR. Table 2 summarizes the RT−FTIR results. It is evident that all the onium borates initiated photopolymerization of the epoxide. In particular, **IFB**, **SFB5**, and **PyFB2** served as efficient cationic photoinitiators. **IFB** showed the highest R_p value. However, the degree of conversion for **IFB** was slightly lower than that of **SFB5**. Since **PyFB2** absorbs light above 365 nm as shown in Figure 2, it would give a high R_p value. The R_p value for **SFB1** was lower than half for **IFB**. This contrasts the result of the spectral sensitivity. Since the spectral sensitivity results from

Table 2. Rate of Polymerization (R_p) and Degree of Conversion on the Photopolymerization of an Epoxide (ERL-4221) in a PMMA Film by Direct Photolysis of the Onium Tetrakis(pentafluorophenyl)borates[a]

initiator	R_p (10^2 M/s)	conversion[b] (%)
IFB	63	70
SFB1	33	65
SFB2	5.9	45
SFB3	25	65
SFB4	11	47
SFB5	58	74
PyFB1	4.3	45
PyFB2	46	61

[a] [initiator] = 7.7×10^{-2} M in the mixture of ERL-4221 and PMMA (w/w = 1/1). Light intensity = 800 W/m^2 (254 nm). [b] Degree of conversion at 60 s after light irradiation.

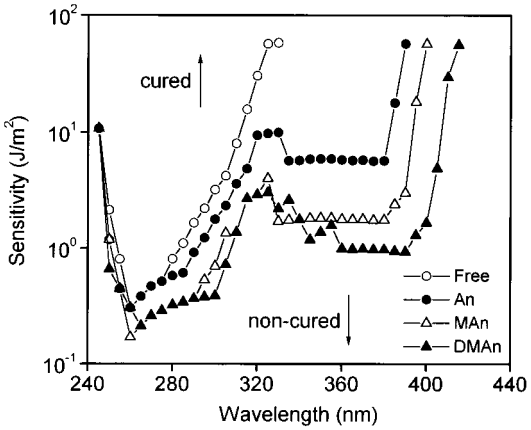


Figure 6. Spectral sensitivity of the poly(MMA-*co*-M100) film containing 7.7×10^{-2} M **SFB** and 7.7×10^{-2} M anthracene sensitizers (**An**, anthracene; **MAn**, 9-methylanthracene; **DMAn**, 9,10-dimethylanthracene). Film thickness = 10 μm. Exposed to the light from a xenon lamp.

both the degree of conversion and the solubility of a cure to toluene as a developing solvent, one explanation for the higher spectral sensitivity of **SFB1** over **SFB5** may be because the cure for **SFB1** is more soluble than that for **SFB5**. The R_p values for **SFB2**, **SFB3**, **SFB4**, and **PyFB1** were lower than that for **SBF1**. Consequently, the R_p value decreases as follows: **IFB** > **SFB5** > **PyFB2** > **SFB1** > **SFB3** > **SFB4** > **SFB2**, **PyFB1**. The reason for the difference in these R_p values is hypothesized to be that the energy of the light absorbed by each onium borate is different and each onium borate has a different quantum yield of acid generation. The direct photolysis of the onium borates has a mechanism similar to that for the corresponding onium salts.[5,14,23,37]

Photopolymerization by Sensitized Photolysis of Onium Tetrakis(pentafluorophenyl)borates. To increase sensitivity to 365 nm light, anthracenes (**An**, **MAn**, **DMAn**) were used as sensitizers, since they show strong absorption at 365 nm. It was reported that diaryliodonium,[5−14,27] triarylsulfonium,[6−14,16,17] and phenacylsulfonium[21,27] compounds were sensitized by the excited singlet state of anthracene and that photodecomposition occurred by an electron-transfer reaction from the excited singlet state of anthracene to the onium cation in the compounds. Figure 6 shows the spectral sensitivity of the photopolymerizable films of the poly(MMA-*co*-M100) containing **SFB1** with the anthracenes. It is clear that the sensitivity of the photopolymerizable films increased by holding the anthracenes in the 320−400 nm region. The spectral sensitivity corresponds to the absorption spectrum of each anthracene. The spectral sensitivity increases in the order, **DMAn** > **MAn** > **An**. The order is the same order as the quantum yield of acid generation as described in a previous paper.[27] Namely, the quantum yield of the acid generated by the sensitized decomposition of either **SFB1** or **IFB** by the anthracenes increases in the order, **DMAn** > **MAn** > **An**.

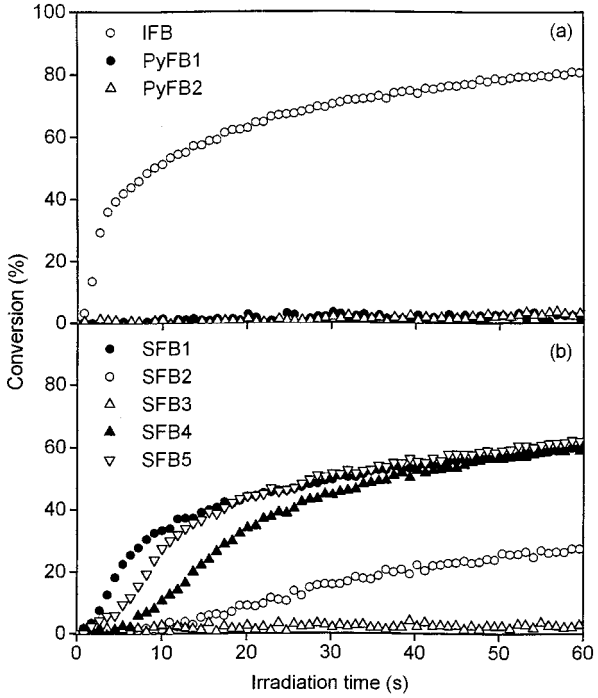


Figure 7. Photopolymerization profiles of an epoxide (ERL-4221) by 9-methyl-anthracene (**MAn**) sensitized photolysis of the onium tetrakis(pentafluorophenyl)borates in a PMMA film recorded by RT−FTIR spectroscopy exposed to the light of a high-pressure mercury lamp. [**MAn**] = 7.7×10^{-2} M: [initiator] = 7.7×10^{-2} M in the mixture of ERL-4221 and PMMA (w/w = 1/1). Light intensity = 960 W/m^2 (365 nm).

Table 3. Rate of Polymerization (R_p) and Degree of Conversion of on the Photopolymerization of an Epoxide (ERL-4221) in a PMMA Film by 9-Methylanthracene (MAn) Sensitized Photolysis of the Onium Tetrakis(pentafluorophenyl)borates[a]

initiator	R_p (10^2 M/s)	conversion[b] (%)
IFB	80	83
SFB1	24	65
SFB2	3.3	28
SFB3	0.13	2.9
SFB4	12	59
SFB5	18	62
PyFB1	0.15	1.6
PyFB2	0.25	2.5

[a] [**MAn**] = 7.7×10^{-2}: [initiator] = 7.7×10^{-2} M in the mixture of ERL-4221 and PMMA (w/w = 1/1). Light intensity = 960 W/m^2 (365 nm). [b] Degree of conversion at 60 s after light irradiation.

Figure 7 shows the **MAn**-sensitized polymerization profiles of epoxide in a PMMA film for comparing the onium borates containing different onium cations by RT−FTIR. Table 3 summarizes the RT−FTIR results. The polymerization profiles by the sensitized photolysis were clearly different from those by the direct photolysis. It was observed that **IFB**, **SFB1**, and **SFB4** initiated photopolymerization in a similar manner as the corresponding onium salts, i.e., diphenyliodonium,[6−8,14] phenacylsulfonium,[21] and dialkyl(4-hydroxy)sulfonium[21] salts. The photopolymerizable film containing **IFB** showed both the highest R_p value and degree of conver-

Scheme 3

$$H^+B(C_6F_5)_4^- \xrightarrow{\Delta} HC_6F_5 + B(C_6F_5)_3$$

sion. When **SFB2** was used as an initiator, its R_p value was one order lower than the values for **IFB**, **SFB1**, or **SFB5**. **SFB3**, **PyFB1**, and **PyFB2** did not initiate any polymerization. Their conversion degrees were less than 3% even after 60s of irradiation. There are several reasons why **SFB3**, **PyFB1**, and **PyFB2** behaved this way: (1) no electron-transfer reaction from the excited singlet state of **MAn** (^{1}**MAn***) to the onium borates occurred; (2) the electron-transfer reaction occurred only formed nonreactive radicals; (3) a back-electron-transfer reaction occurred rapidly after the electron-transfer reaction. As we shall see later, neither **SFB2** nor **SFB3** reacted with ^{1}**MAn***. On the other hand, only **PyFB2** showed a reversible redox wave ($E_{1/2} = -0.62$ V vs SCE). Thus, the stable cation radical of **PyFB2** is formed by the electron-transfer reaction, so that no acid is generated. In addition, pyridine derivatives would also most likely be produced by the decomposition of **PyFB1** and **PyFB2**, and some of the generated acid would be neutralized by the pyridine derivatives. Consequently, the R_p value increases in the order **IFB** > **SFB1** > **SFB5** > **SFB4** ≫ **SFB2** ≫ **SFB3**, **PyFB1**, **PyFB2**.

Thermal Decomposition of the Generated Acid from Onium Tetrakis(pentafluorophenyl)borates. An acid was observed in the irradiated photopolymerizable film containing the onium borates. The acid was stable at room temperature in the film as well as in methanol.[27] Also, the acid was stable in the hexane extract of the film. The acid is most likely $H^+B(C_6F_5)_4^-$ which was supported by the measurement of ^{19}F NMR. This result agrees with that obtained by Castellanos et al.[26] It is interesting that the acid in the film and in the hexane extract disappeared after heating at 100 °C for 10 min. This notable result is explained in Scheme 3.

Thus, the acid, $H^+B(C_6F_5)_4^-$ would decompose to nonacidic compounds, HC_6F_5 and $B(C_6F_5)_3$, by heating. HC_6F_5 was detected by GC/MS and was identified by using an authentic sample. However, it was not detected without heating. From these results, the acid would likely decompose by heating rather than by irradiating light. Trace amounts of the acid have determined from the irradiated photopolymerizable film containing **PyFB1** and **PyFB2**. Probably, part of the generated acid would be neutralized by the simultaneously generated pyridine derivatives. This finding supports that **PyFB1** and **PyFB2** most probably did not initiate polymerization. When the corresponding onium salts containing counteranions such as PF_6^- and BF_4^- were used as initiators, the generated acids, $H^+PF_6^-$ and $H^+BF_4^-$, did not decompose by heating, since these acids are thermally stable.[27]

Free Energy Changes and Fluorescence Quenching of 9-Methylanthracene by the Onium Tetrakis(pentafluorophenyl)borates. In a previous paper,[27] we reported that the fluorescence of the anthracene was quenched by **IFB** and **SFB1** and that the fluorescence quenching is based on an electron-transfer reaction from the excited singlet state of the anthracenes to the onium cation in **IFB** and **SFB1**. Namely, the anthracenes and these onium borates serve as a donor and an acceptor, respectively. In the present study, we would like to focus on the **MAn**/onium borate photoinitiator systems. It was observed that the fluorescence of **MAn** was quenched by **IFB**, **SFB1**, **SFB4**, **SFB5**, and **PyFB1**.

Table 4. Reduction Potential of the Onium Tetrakis(pentafluorophenyl)borates (E_{red}), Free Energy Change (ΔG^S) and Fluorescence Quenching Rate Constant (k_q) of the Excited Singlet State of 9-Methylanthracene (MAn) by the Onium Tetrakis(pentafluorophenyl)borates

initiator	cation part	E_{red}[a] (V vs SCE)	ΔG^S[b] (kJ/mol)	k_q[c] (10^{-9} M^{-1} s^{-1})
IFB	Ph_2I^+	−0.64[d]	−144	14
SFB1	$Me_2S^+CH_2COPh$	−0.87	−123	12
SFB2	$Me_2S^+CH_2Ph$	−1.21	−89	*e*
SFB3	*p*-$HOC_6H_4S^+Me_2$	*f*		*e*
SFB4	*p*-$MeCOOC_6H_4S^+Me_2$	−1.11	−99	3.1
SFB5	*p*-$HOC_6H_4(Me)S^+CH_2Ph$	−1.30	−81	4.9
PyFB1	$C_5H_5N^+-CH_2COPh$	−1.29	−82	5.0
PyFB2	4-$NCC_5H_4N^+-CH_2COPh$	−0.62[g]	−146	

[a] Stand for the peak potentials. [b] Calculated by eq 4, the oxidation potential (0.797 V vs $Ag/AgNO_3$),[45] and the excited singlet energy (74.1 kcal/mol).[46] [c] Calculated by eq 5 and the fluorescence lifetime of **MAn** τ_0 (=3.99 ns) in areated MeOH solution. [d] From ref 13, since the reduction potential was not detectable. [e] No quenching. [f] Not detectable. [g] Stands for the redox potential.

The free energy change (ΔG_{et}) on a photoinduced electron-transfer reaction is given by the Rehm−Weller equation (eq 3),[41] where $E_{ox}(D/D^{+\bullet})$ is the oxidation

$$\Delta G_{et} = E_{ox}(D/D^{+\bullet}) - E_{red}(A^{-\bullet}/A) - E - Ze^2/\epsilon\alpha \quad (3)$$

potential of the donor, $E_{red}(A^{-\bullet}/A)$ is the reduction potential of the acceptor, E is the excited energy of the sensitizer, and $Ze^2/\epsilon\alpha$ is the Coulombic energy, the free energy gained by the radical ions formed at a distance, α, in a solvent with the dielectric constant ϵ. To obtain ΔG^S between ^{1}**MAn*** and the onium borates, we approximated eq 3 to eq 4 as follows:

$$\Delta G^S = E_{ox}(\mathbf{MAn}/\mathbf{MAn}^{+\bullet}) - E_{red}(On^{\bullet}/On^{+}) - E_{00} \quad (4)$$

Here $E_{ox}(\mathbf{MAn}/\mathbf{MAn}^{+\bullet})$ is the oxidation potential of **MAn** (=0.797 V vs $Ag/AgNO_3$),[42] $E_{red}(On^{\bullet}/On^{+})$ is the reduction potential of the onium cation in the onium borates, and E_{00} is the excited singlet energy of **MAn** (=74.1 kcal/mol).[43] On the other hand, the fluorescence quenching rate constant (k_q) of **MAn** by the onium borates is estimated by the Stern−Volmer relationship (eq 5),

$$I_{F0}/I_F = 1 + K_{SV}[Q] \quad K_{SV} = k_q\tau_0 \quad (5)$$

where I_{F0} and I_F are the fluorescence intensities in the absence and presence, respectively, of the onium borates being used as a quencher Q, K_{SV} is the Stern−Volmer constant, [Q] is the concentration of the onium borates, and τ_0 (=3.99 ns) is the fluorescence lifetime of **MAn** in the absence of the onium borates in an areated MeOH solution.[27]

Table 4 summarizes the ΔG^S and k_q values. **IFB** gave the most negative ΔG^S value and showed the highest k_q values as compared to the other onium borates. It was observed that neither **SFB2** nor **SFB3** quenched the fluorescence of **MAn**. These findings suggest that no electron-transfer reaction from ^{1}**MAn*** to both of the onium borates occurred. Hence, both **SFB2** and **SFB3** most likely did not initiate polymerization. On the other hand, **PyFB1** probably did not initiate polymerization, despite the fact that it quenched the fluorescence of **MAn**. Since the absorption of **PyFB2** overlapped that of **MAn**, we were able to carry out a quenching experiment using **PyFB2**. As we mentioned earlier, both

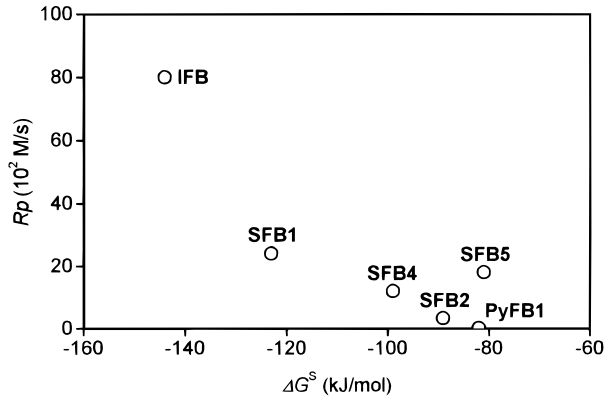


Figure 8. Comparison of the rate of polymerization (R_p) with free energy change (ΔG^S) for the 9-methylanthracene/onium tetrakis(pentafluorophenyl)borate photoinitiator systems.

PyFB1 and **PyFB2** did not initiate polymerization, since both probably produced the corresponding pyridine derivatives by self-decomposition which in turn neutralized a part of the generated acid. Figure 8 compares the R_p values with the ΔG^S values for the **MAn**/onium borate photoinitiator systems. It was observed that the R_p values roughly increased when the ΔG^S values decreased. We observed similar results in the radical photopolymerization of an acrylate by the styryl dye/sulfonium butyltriphenylborate photoinitiator systems.[45] We suppose that these observations will be useful in the development of more efficient photoinitiator systems.

Conclusion

In this paper, we researched the effect of the different cations of the onium tetrakis(pentafluorophenyl)borates on cationic photopolymerization. We observed the different photopolymerization profiles between the direct photolysis and the sensitized photolysis of the onium borates. In the sensitized polymerization using 9-methylanthracene as a sensitizer, it was found that the R_p values increase with decreasing ΔG^S values. The acid generated by the decomposition of the onium borates further decomposes to nonacidic compounds by heating, which implies that the onium borates are useful for applications such as metal coating and electronic devices.

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