Substituted Cyclopropenium Salts as Photoinitiators for Cationic Polymerization of Glycidyl Phenyl Ether

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ABSTRACT: A new series of triarylcyclopropenium tetrakis(pentafluorophenyl)gallates (**I**) were synthesized by anion exchange. These salts are photoacid generators from which we have measured the rates of acid release using the indicator Quinaldine Red (QR). Electron-donating substituents on the aromatic ring slow the rate of photoacid release. Cationic photopolymerization of glycidyl phenyl ether (GPE) was also examined. With 1 wt % triphenylcyclopropenium (TPCP) gallate, 90% of conversion of GPE was achieved within 20 min irradiation at 300 nm. The polymerization afforded polyGPE with M_w of 4100−8100. The initiating species was identified as a proton produced from photolysis of the triarylcyclopropenium cation.

Introduction

Research on photoinitiators to catalyze the cationic polymerization of vinyl ethers and epoxides has rapidly accelerated due to the various uses of these monomers in industry in sectors ranging from coatings and adhesives to printing inks.[2] The most successful commercial initiators are iodonium and sulfonium salts paired with poorly nucleophilic anions, such as PF_6^-, SbF_6^-, and AsF_6^-.[3] A few years ago Fouassier's group achieved significant improvement in initiator performance through the synthesis of iodonium salts paired with tetrakis(perfluorophenyl)borate counterion.[4] Our group has recently developed a new anion, tetrakis(pentafluorophenyl)gallate, $Ga(C_6F_5)_4^-$, and paired this with iodonium and sulfonium salts forming a new series of photoinitiators.[5,6] These photoinitiators showed excellent performance which matched, or in some cases exceeded, that of the diaryliodonium tetrakis(pentafluorophenyl)borates.

Compounds in the cyclopropenium series, of which triphenylcyclopropenium (TPCP) is an example, were first synthesized and described by Breslow and coworkers.[7] Constructed from the smallest aromatic ring, the reduction potential of the TPCP cation is measured in acetonitrile to be −0.75 V vs SCE,[8] indicating a high thermodynamic stability for the ground state. We thought TPCP a potentially interesting cation with which a cascade of nonnucleophilic anions might be paired for investigation as photochemical superacid sources. We have recently reported that triphenylcyclopropenium (TPCP) tetrakis(pentafluorophenyl)gallate is a good thermal initiator for the cationic polymerization of glycidyl phenyl ether (GPE) when used with cyclohexanone.[9] Since it is poorly soluble in epoxy resins, this new initiator afforded limited photopolymerization of standard epoxy resins such as epoxy-functionalized silicones. However, TPCP tetrakis(pentafluorophenyl)gallate dissolves completely in glycidyl phenyl ether (GPE) and initiates its photopolymerization when irradiated at 300 nm. A new series of triarylcyclopropenium tetrakis(pentafluorophenyl)gallates (Figure 1) have been synthesized, and we report their use as photoinitiators for the cationic polymerization of GPE.

Experimental Section

Materials. All chemicals were used as received from Aldrich unless otherwise noted. $CHCl_3$ was treated with concentrated sulfuric acid and distilled over P_2O_5. Acetonitrile (HPLC grade) and CH_2Cl_2 were used as received. Quinaldine Red (OR) was purchased from Acros Organics. Octyl phenyl ether was prepared according to a literature procedure.[10] Lithium tetrakis(pentafluorophenyl)gallate was prepared as previously reported.[5] TPCP tetrakis(pentafluorophenyl)gallate (**I$_a$**) and diphenyl-(2-methoxynaphthyl-1)cyclopropenium tetrakis(pentafluorophenyl)gallate (**I$_e$**) were prepared as previously reported.[11]

Measurements. ^{1}H and ^{19}F NMR spectra were recorded with either a Varian Gemini 200 NMR or a Varian Unity plus 400 NMR spectrometer. Chemical shifts are in ppm with TMS as the internal standard (^{1}H NMR) or $CFCl_3$ as the external standard (^{19}F NMR). Melting points were determined with a Thomas-Hoover capillary melting point apparatus and were uncorrected. MS measurements were carried out on a Shimadzu GCMS-QP5050 mass spectrometer with a DI-50 direct sample inlet device. UV−vis spectra were recorded on a HP 8452A diode array UV−vis spectrometer. Number- and weight-average molecular weights (M_n and M_w) and polydispersity ratios (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a Shimadzu HPLC system equipped with a Plgel 5 μm MIXED-C 300X7.5 mm column (Polymer Laboratories), using THF as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration, and a RID-10A refractive index (RI) detector. Irradiations were carried out in the Rayonet photochemical reactor (16 300 nm lamps) equipped with a jacketed beaker (Pyrex). Thin-layer chromatography was performed with Whatman silica gel-coated TLC plates. Atlantic Microlab Inc. produced the elemental analyses. The University of Illinois, Champaign School of Chemical Science, mass spectrometry laboratory determined the HRMS.

Synthesis of Tri-*p*-fluorophenylcyclopropenium Gallate (I$_b$). To a suspension of tri-*p*-fluorophenylcyclopropenium trifluoromethanesulfonate[12] (0.141 g, 0.3 mmol) in acetonitrile (3 mL) was added a solution of lithium tetrakis(pentafluorophenyl)gallate (0.357 g, 0.4 mmol) in acetonitrile (5 mL). The mixture was stirred for 30 min at room temperature or until the TLC showed no starting material remained. Dichloromethane (50 mL) was added, and the solution was washed with water (30 mL) and then brine. After drying over $MgSO_4$,

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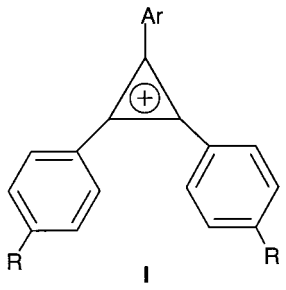


I

Compd.	R	Ar
Ia	H	phenyl
Ib	F	4-fluorophenyl
Ic	OMe	anisyl
Id	OC_8H_{17}-*n*	*p* - octoxyphenyl
Ie	H	2-methoxynaphthyl-1-

Figure 1. Structure of triarylcyclopropenium tetrakis(pentafluorophenyl)gallates.

the filtrate was concentrated to give a yellowish solid, which was purified by silica gel chromatography using CH_2Cl_2−pentane as the eluent. This was followed by recrystallization from CH_2Cl_2−hexane twice affording a colorless crystal (0.123 g) (38.7%); mp 184−185 °C. ^{1}H NMR ($CDCl_3$−CD_3CN): δ 8.53, 8.50 (dd, $^3J_{H-H}$ = 8.4 Hz, 6H, 2,6-H on phenyl), 7.62, 7.58 (dd, $^3J_{H-H}$ = $^3J_{F-H}$ = 8.4 Hz, 6H, 3,5-H on phenyl). ^{19}F NMR ($CDCl_3$): δ −91.28 (4-F on phenyl), −123.63 (d, 2,6-F on C_6F_5), −158.96 (sm, 4-F on C_6F_5), −164.18 (sm, 3,5-F on C_6F_5). Anal. Calcd for $C_{45}H_{15}F_{23}Ga\cdot H_2O$: C, 50.17; H, 1.31. Found: C, 50.30; H, 1.39. MS: m/s 570.55 (3.19, $Ga(C_6F_5)_3$); 488.25 (100, $C_{21}H_{12}F_3$−C_6F_5); 321.10 (23.38, $C_{21}H_{12}F_3$). HRMS: calcd for $C_{21}H_{12}F_3$: m/s 321.089 110. Found: 321.089 200.

Synthesis of Trianisylcyclopropenium Gallate (I_c). To a suspension of tetrachlorocyclopropene (0.45 g, 2.5 mmol) and aluminum chloride (0.367 g, 2.75 mmol) in $CHCl_3$ (7 mL) was added a solution of anisole (0.811 g, 7.5 mmol) in $CHCl_3$ (3 mL) at 0 °C during 20 min. After the addition, the mixture was heated to reflux for 40 min (a yellow solid was present). The reaction mixture was next cooled and poured into 20 mL of ice water. The yellow solid was obtained by filtration (0.36 g) (37%); mp 178 °C (decomposed). ^{1}H NMR (DMSO-d_6): δ 8.58 (d, $^3J_{HH}$ = 8.4 Hz, 6H, 2,6-H on phenyl), 7.41 (d, $^3J_{HH}$ = 8.4 Hz, 6H, 3,5-H on phenyl) 4.04 (s, 9H, OCH_3).

To a suspension of the above solid (0.146 g, 0.37 mmol) in CH_3CN (3 mL) was added a solution of lithium tetrakis(pentafluorophenyl)gallate (0.392 g, 0.44 mmol) in acetonitrile (3 mL). The mixture was stirred for 1 h at room temperature. After workup, a white crystal (0.18 g) was obtained with yield of 45.0%; mp 205−207 °C. ^{1}H NMR ($CDCl_3$): δ 8.24 (d, $^3J_{H-H}$ = 8.4 Hz, 6H, 2,6-H on phenyl), 7.24 (d, $^3J_{H-H}$ = 8.4 Hz, 6H, 3,5-H on phenyl), 4.01 (s, 9H, OCH_3). ^{19}F NMR($CDCl_3$): δ −123.67 (d, 2,6-F on C_6F_5), −159.23 (sm, 4-F on C_6F_5), −164.50 (sm, 3,5-F on C_6F_5). Anal. Calcd for $C_{48}H_{21}F_{20}O_3Ga\cdot H_2O$: C, 51.78; H, 2.08. Found: C, 51.66; H, 1.94. MS: m/s 570.05 (20.12, $Ga(C_6F_5)_3$); 542.25 (100, $C_{24}H_{21}O_3$−C_6F_5); 357.10 (22.01, $C_{24}H_{21}O_3$). HRMS: calcd for $C_{24}H_{21}O_3$: m/s 357.149 070. Found: 357.149 200.

Synthesis of Tri-*p*-octoxyphenylcyclopropenium Gallate (I_d). To a suspension of tetrachlorocyclopropene (0.45 g, 2.5 mmol) and aluminum chloride (0.367 g, 2.75 mmol) in $CHCl_3$ (8 mL) was added a solution of octyl phenyl ether (1.55 g, 7.5 mmol) in $CHCl_3$ (3 mL) at 0 °C during 10 min. After addition, the mixture was heated to reflux for 3 h and then cooled and poured into 20 mL of ice water. The organic phase was separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic phases were washed with brine and dried over $MgSO_4$. Removal of the solvent gave a brown oil.

The brown oil above was dissolved in CH_3CN−CH_2Cl_2 (2:1/15 mL). To this solution was added a solution of sodium hexafluoroantimonate (0.645 g, 2.5 mmol) in CH_3CN (5 mL). The mixture was stirred for 2 h at room temperature. The solvent was removed and the residue was dissolved in CH_2Cl_2 (20 mL), washed with water and brine, and dried over $MgSO_4$. The concentrated dark oil was purified by silica gel column using CH_2Cl_2 as the eluent. After washing completely with ether, tri-*p*-octoxyphenylcyclopropenium hexafluoroantimonate (0.327 g) was obtained as a white solid (14.7%); mp 123−124 °C. ^{1}H NMR ($CDCl_3$): δ 8.15 (d, d, $^3J_{H-H}$ = 7.4 Hz, 6H, 2,6-H on phenyl), 7.20 (d,d $^3J_{H-H}$ = 7.4 Hz, 6H, 3,5-H on phenyl), 4.08 (m, 6H, OCH_2), 1.84 (m, 6H, CH_2), 1.34 (broad, 30H, $(CH_2)_5$), 0.92 (m, 9H, CH_3).

To a solution of tri-*p*-octoxyphenylcyclopropenium hexafluoroantimonate (0.1775 g, 0.2 mmol) in CH_2Cl_2 (10 mL) was added a solution of lithium tetrakis(pentafluorophenyl)gallate (0.214 g, 0.24 mmol) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred for 2 h. The solution was washed with water and brine and dried over $MgSO_4$. Removal of solvent gave a viscous oil (0.30 g), which was purified by silica gel column using CH_2Cl_2−hexane as the eluent to afford the product (0.236 g) as a waxy solid with yield of 84.9%. ^{1}H NMR ($CDCl_3$): δ 8.21 (d, $^3J_{H-H}$ = 8.6 Hz, 6H, 2,6-H on phenyl), 7.20 (d,d, $^3J_{H-H}$ = 8.6 Hz, 6H, 3,5-H on phenyl), 4.14 (t, $^3J_{H-H}$ = 6.4 Hz, 6H, OCH_2), 1.88 (m, 6H, CH_2), 1.55−1.29 (m, 30H, $(CH_2)_5$), 0.90 (m, 9H, CH_3). ^{19}F NMR ($CDCl_3$): δ −123.35 (d, 2,6-F on C_6F_5), −159.05 (sm, 4-F on C_6F_5), −164.21 (sm, 3,5-F on C_6F_5). Anal. Calcd for $C_{69}H_{63}F_{20}O_3Ga$: C, 59.63; H, 4.39. Found: C, 59.90; H, 4.57.

General Procedure To Measure the Rate of Acid Release. Solutions of triarylcyclopropenium gallates (1×10^{-3} M) in acetonitrile containing ~10 ppm of Quinaldine Red were prepared. The initial absorbance of these solution at 520 nm was ~0.9. The solutions thus prepared were irradiated with a Rayonet photochemical reactor, and the absorbance of QR at 520 nm was measured.

General Procedure of the ^{1}H NMR Monitored Polymerization. Glycidyl phenyl ether (0.50 g) (GPE) containing 0.25−2 wt % initiator was placed in a vial (Pyrex) equipped with a stirring bar and irradiated with a Rayonet photochemical reactor. After a fixed time, the reaction mixture was diluted with CH_2Cl_2. The mixture was then poured into methanol to precipitate the polymer. This was separated from the supernatant by decantation and dried in vacuo. The conversion of GPE was estimated by ^{1}H NMR spectroscopy before precipitation from methanol. The signals at 2.76−2.93 ppm were monitored and integrated as a function of time. The signals at 6.90−7.33 ppm were used as internal standard, and conversion was calculated from the following equation:

$$\text{conversion} = 1 - \frac{\left[\frac{I_{2.76-2.93}}{I_{6.90-7.33}}\right]_t}{\left[\frac{I_{2.76-2.93}}{I_{6.90-7.33}}\right]_0} \qquad (1)$$

Results and Discussion

Initiator Synthesis. Triarylcyclopropenium gallates were synthesized by anion exchange with lithium tetrakis(pentafluorophenyl)gallate using the corresponding triarylcyclopropenium hexafluoroantimonate, trifluoromethanesulfonate, or chloride. ^{1}H NMR, ^{19}F NMR, mass spectrometry, and elemental analysis confirmed the structures. Each of the gallates is white solid or crystals stable in air at room temperature though they decompose modestly in solution. Each exhibits strong UV absorption in acetonitrile and is easily photodecomposed with UV irradiation to produce an acid[11] that can

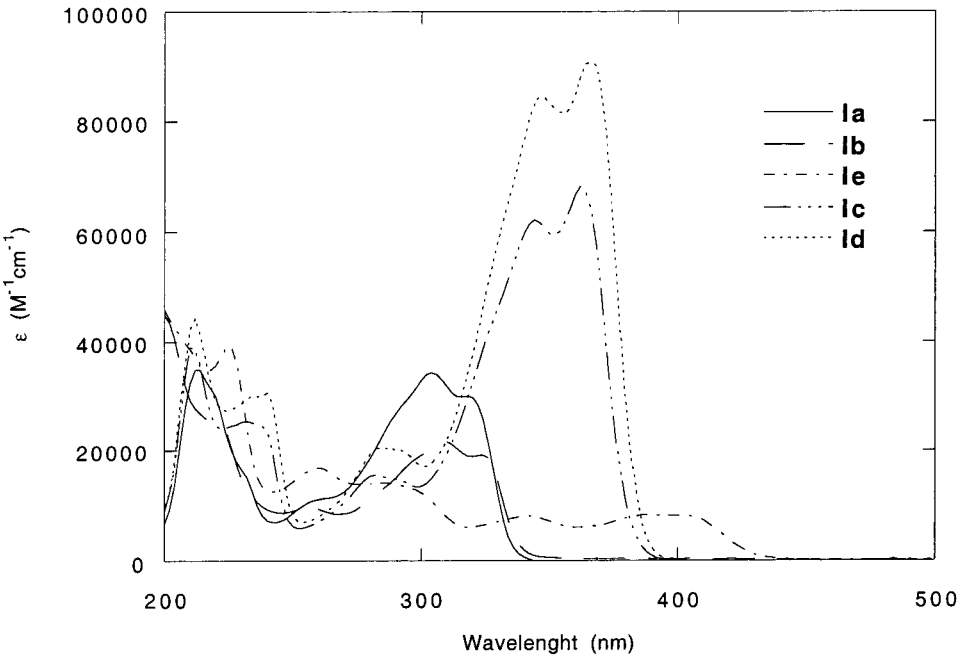


Figure 2. UV−vis spectra of triarylcyclopropenium gallates: $\mathbf{I_a}$, $\mathbf{I_b}$, $\mathbf{I_c}$, $\mathbf{I_d}$, and $\mathbf{I_e}$ in acetonitrile (2×10^{-5} M).

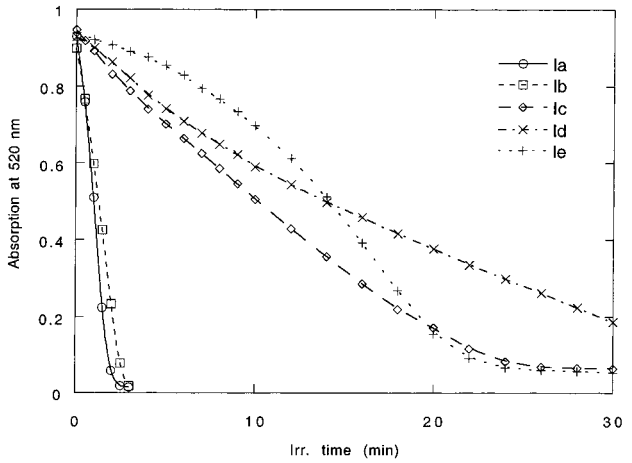


Figure 3. Formation of photoacid from triarylcyclopropenium gallates. Bleaching of QR (~10 ppm) at 520 nm by $\mathbf{I_a}$, $\mathbf{I_b}$, $\mathbf{I_c}$, $\mathbf{I_d}$, and $\mathbf{I_d}$ in acetonitrile (1×10^{-3} M).

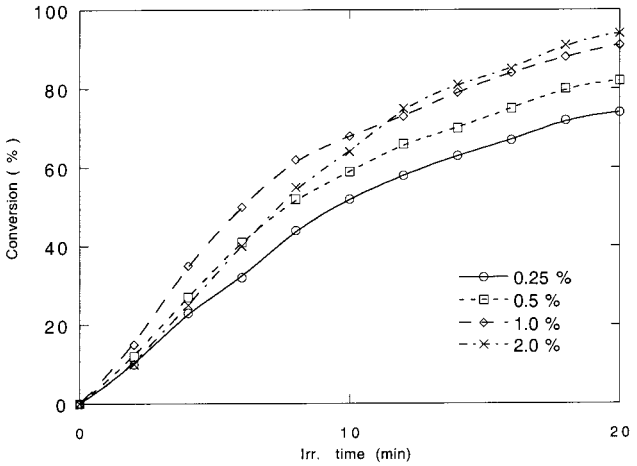


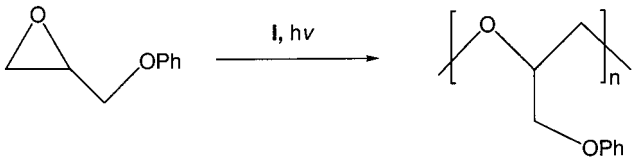
Figure 4. Conversion vs irradiation time for the photopolymerization of GPE by $\mathbf{I_a}$: different ratios (0.25, 0.50, 1.0, and 2.0 wt %) of $\mathbf{I_a}$ to GPE.

initiate the polymerization of GPE. The UV−vis spectra of the triarylcyclopropenium gallates are shown in Figure 2.

Acid Release. Photolysis of triarylcyclopropenium gallates produced an acid[11] that initiated the cationic polymerization of GPE. Direct measurement of the formation of the photoacid offers a quick way to measure the photoreactivity of triarylcyclopropenium gallates. A new method has been recently developed by our group[6] to determine the acidity in nonaqueous systems. Quinaldine Red (QR) is used as the pH indicator with an UV−vis absorption at visible band of 520 nm in acetonitrile. The bleaching of QR at 520 nm was monitored as acid was produced during irradiation (Figure 3). Each of the newly synthesized triarylcyclopropenium gallates is a photoacid generator. Electron-donating substituents on the aromatic ring slow the photoacid release rate when compared to $\mathbf{I_a}$ or $\mathbf{I_b}$ gallates.

Polymerization of GPE by Triarylcyclopropenium Gallates. Polymerization of GPE with triarylcyclopropenium gallates (0.25−2 wt %) was carried out at room temperature. The triarylcyclopropenium gallates were completely soluble in GPE at ambient temperature, but GPE did not polymerize at all under similar conditions when maintained for 48 h in dark. Upon irradiation in a Rayonet photochemical reactor, polymerization of GPE proceeded rapidly to afford the polymers with M_w of 4100−8100 (Scheme 1, Figures 4 and 5, Table 1). The conversion of GPE increased as the ratio of triphenylcyclopropenium tetrakis(pentafluorophenyl)gallate to GPE increased and reached a maximum at a ratio of 1 wt % (Figure 4). With 1 wt % of $\mathbf{I_a}$, over 90% of conversion of GPE was achieved within 20 min irradiation. An increase in the ratio of $\mathbf{I_a}$ to GPE did not increase the conversion.

Scheme 1. Photopolymerization of GPE by Triarylcyclopropenium Gallates (I)



Scheme 2. Cationic Polymerization of GPE by Triarylcyclopropenium Gallates (I)

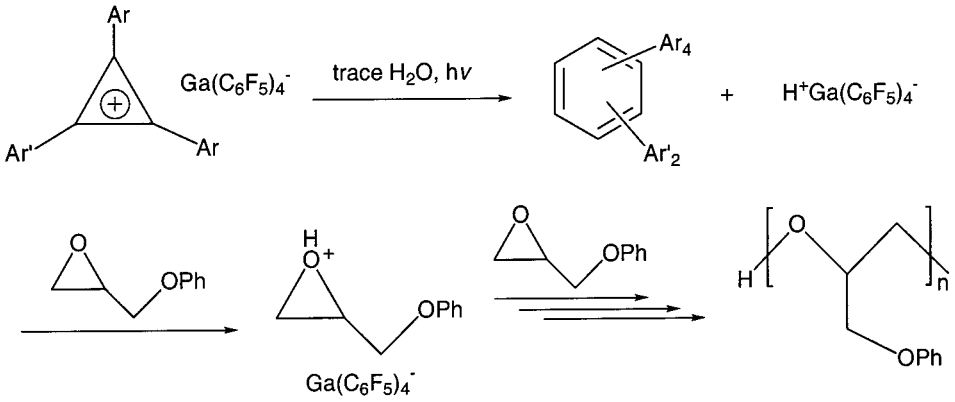


Table 1. Photopolymerization of GPE by Triarylcyclopropenium Gallates (1 wt %)

initiator	irrad time (min)	conv[a] (%)	yield[b] (%)	M_w[c]	PD
$\mathbf{I_a}$	5	25	15	4500	1.239
	10	55	43	5000	1.420
	20	90	80	7300	1.784
$\mathbf{I_b}$	5	40	34	4800	1.364
	10	70	65	6000	1.512
	20	95	91	8100	1.701
$\mathbf{I_c}$	5	26	20	4000	1.247
	10	52	42	4700	1.310
	20	77	70	5600	1.517
$\mathbf{I_d}$	5	23	18	4100	1.235
	10	48	46	5000	1.374
	20	76	69	5400	1.484
$\mathbf{I_e}$	5	30	22	4600	1.295
	10	56	54	5200	1.380
	20	86	77	6600	1.585

[a] Determined by ^{1}H NMR. [b] Methanol-insoluble. [c] Estimated by GPC based on a polystyrene standard samples.

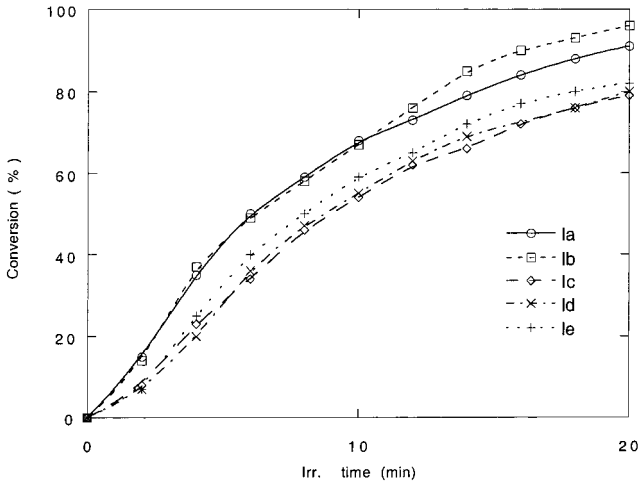


Figure 5. Conversion vs irradiation time for the photopolymerization of GPE by triarylcyclopropenium gallates: $\mathbf{I_a}$, $\mathbf{I_b}$, $\mathbf{I_c}$, $\mathbf{I_d}$, and $\mathbf{I_e}$ (1 wt %).

Initiator activity was determined by using 1 wt % of initiator (Figure 5 and Table 1). With an increase in the irradiation time, the conversion and yields of GPE increased, and the molecular weight and the polydispersity of the resulting polymer increased as well. Electron-donating substituents on the aromatic ring decrease initiator activity. The activity order was $\mathbf{I_b} \sim \mathbf{I_a} > \mathbf{I_e} > \mathbf{I_c} \sim \mathbf{I_d}$, similar to that of photoacid release.

Mechanism. ^{1}H NMR spectroscopy of the polymers obtained showed no triarylcyclopropenium signals, supporting the notion that a proton was the actual initiating species (Scheme 2). ^{19}F NMR spectroscopy of the polymer formed from $\mathbf{I_b}$ also showed no fluorophenyl signals. This provides additional evidence that the initiating species was not derived from the cyclopropenium salt.

In summary, a new series of triarylcyclopropenium gallates were synthesized. These gallates are photoacid generators and useful photointiators for the cationic polymerization of GPE. The polymerization proceeds rapidly, affording polyGPE with M_w of 4100−8100. The initiating species was identified as a proton produced by photolysis of triarylcyclopropenium cations.

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(12) Weiss, R.; Kölbl, H.; Schlierf, C. *J. Org. Chem.* **1976**, *41*, 2258. ^{1}H NMR (CD_3CN): δ 8.99, 8.96(dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{FH}$ = 5.0 Hz, 2,6-H on phenyl), 7.77, 7.73 (dd, $^3J_{HH}$ = 8.8 Hz, 3,5-H on phenyl). ^{19}F NMR (CD_3CN): δ −74.53 (CF_3SO_3), −91.10 (4-F on phenyl).

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