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Triphenylcyclopropenium hydroxytris(pentafluorophenyl)borate salt for solvent free epoxy curing

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ABSTRACT

A triphenylcyclopropenium salt paired with hydroxytris(pentafluorophenyl)borate counter ion was synthesized as an initiator for cationic polymerization and its activity was compared with triphenylcyclopropenium hexafluoroantimonate. Triphenylcyclopropenium hydroxytris (pentafluorophenyl)borate exhibits excellent activity as a room temperature thermal initiator for epoxide polymerization under solvent free conditions, due to excellent solubility in epoxy resins.

1. Introduction

Salts of stable organic cations such as diaryliodonium [1-4] and triarylsulfonium [4-9] provide useful initiators for cationic polymerization when paired with non-nucleophilic counter ions. In the most commonly used salts, the counter ion is the inorganic anion, SbF_6. However, these salts are hydroscopic and insoluble in nonpolar monomers. Unlike SbF_6^-, the highly stable tetrakis(pentafluorophenyl)borate anion, ($B(C_6F_5)_4^-$), provides salts that are quite soluble in nonpolar monomers [4] and thus assume some commercial value in certain segments of this marketplace.

The anion, hydroxytris(pentafluorophenyl)borate ($HOB(C_6F_5)_3^-$), which was first reported in 1993 [10] shows unique activity in comparison to $B(C_6F_5)_4^-$. We previously reported a new light induced group transfer reaction in $HOB(C_6F_5)_3^-$ [11]. Upon irradiation of *N*-methylisoquinolinium hydroxytris(pentafluorophenyl)borate, a C_6F_5 group was transferred from $HOB(C_6F_5)_3^-$ to the *N*-methylisoquinolinium cation [11]. Unlike $B(C_6F_5)_4^-$, the $HOB(C_6F_5)_3^-$ is capable of protonating the Zr-Me bond in the Cp_2ZrMe_2 complex [12]. Various salts of $HOB(C_6F_5)_3^-$ have previously been used as a co-catalyst in alkene polymerization [13]. However, $HOB(C_6F_5)_3^-$ has not been utilized in cationic polymerization. Due to its unique activities, we decided to explore $HOB(C_6F_5)_3^-$ as a counter ion in cationic polymerization initiators and compare its activity to SbF_6^-.

Triphenylcyclopropenium (TPCP) ion, the smallest Hückel aromatic system, has a reduction potential of -0.75 V *vs* SCE [14]. Triphenylcyclopropenium salts paired with various counter ions including $B(C_6F_5)_4^-$ and SbF_6^- have been synthesized [15]. When combined with a co-initiator such as a carbonyl compound or alcohol, they are effective initiators for thermal epoxy curing [15]. It has been demonstrated that (TPCP) is an effective cation for thermal initiation of cationic polymerization of glycidyl phenyl ether, when paired with $Ga(C_6F_5)_4^-$ [16]. [TPCP] [$Ga(C_6F_5)_4$] requires cyclohexanone to form the actual initiating species [16]. In the presence of trace amounts of water, [TPCP] [$Ga(C_6F_5)_4$] also acts as a photoinitiator in polymerization of glycidyl phenyl ether [17]. [TPCP] [$B(C_6F_5)_4$] also has been shown to act as an activator in metallocene catalyzed polymerization of ethylene and styrene [18]. In this paper, the synthesis of the triphenylcyclopropenium salt paired with hydroxytris(pentafluorophenyl)borate (Figure 1) and its activity as cationic initiator are discussed.

2. Experimental

2.1. Instrumentation

^1H NMR spectra were recorded on a Varian 400 MHz NMR spectrometer and a 300 MHz JEOL nuclear magnetic resonance spectrophotometer in $CDCl_3$ or CD_3CN. Data are reported as follows: multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m = multiplet, br = broad). ^{13}C NMR spectra were recorded on a Varian-400 (100 MHz) NMR spectrometer or a JEOL-300 (75 MHz) spectrometers. ^{19}F NMR spectra and ^{11}B NMR spectra were referenced externally to $CFCl_3$ and $BF_3.OEt_2$, respectively. Chemical shifts are reported in parts per million (ppm), in $CDCl_3$ or CD_3CN, using TMS as the internal reference (0.00 ppm). Melting point was recorded using a Thermo Scientific melting point apparatus and is uncorrected. FT-IR spectra were recorded on a Thermo Nicolet NEXUS 670 FT-IR spectrophotometer. High resolution mass spectra of the new compounds were obtained at the Department of Chemistry, University of Illinois at Urbana-Champaign. Elemental analysis was performed by the Atlantic Microlab., Inc., Norcross, Georgia.

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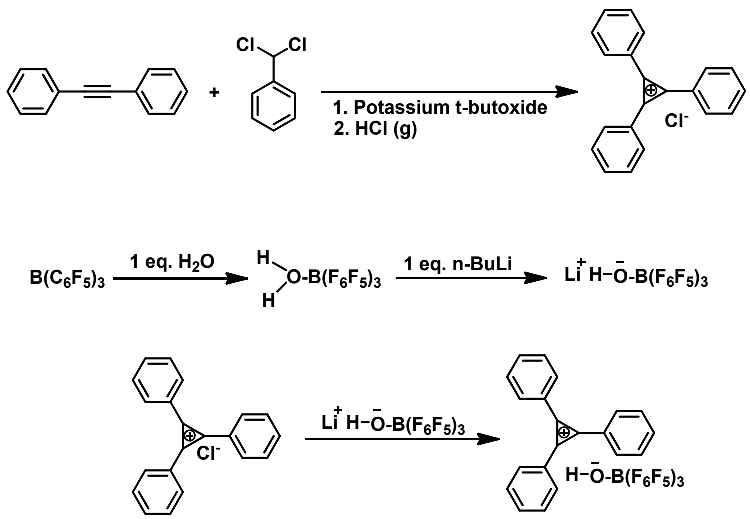

Figure 1. Synthesis of triphenylcyclopropenium salts.

2.2. Materials

All chemicals were purchased from Aldrich, unless otherwise stated. Epoxy monomer, poly BD®605E, was purchased from Sartomer. Triphenylcyclopropenium chloride was synthesized by a modified literature procedure [19]. $H_2O.B(C_6F_5)_3$ was synthesized according to a literature procedure [10]. UV9300 and UV9315 were obtained from General Electric Silicones. Benzal chloride ((dichloromethyl) benzene) was dried over $CaSO_4$ and distilled under vacuum before use. Solvents (Diethyl ether, THF and hexane) were distilled under argon over sodium-benzophenone prior to use, and dichloromethane was distilled over CaH_2 before use. Distilled water was de-oxygenated by purging with argon for 15 min before use. NMR solvents used in irradiation experiments were dried over 4 Å molecular sieves.

2.3. Synthesis

2.3.1. Triphenylcyclopropenium chloride (1)

Diphenylacetylene (4.46 g, 25.20 mmol) was mixed with potassium *t*-butoxide (7 g, 62.38 mmol) and dry benzene (100 mL). To this mixture, benzal chloride (4.84 g, 30.05 mmol) was added and then refluxed for 3h under argon. After cooling to room temperature (RT), water was added and the aqueous layer was extracted with ether (2 x 50 mL). The ether extracts were combined with the benzene solution, dried over $MgSO_4$, and saturated with HCl (g). The crude yellow precipitate thus formed was washed with ether, dried under vacuum and recrystallized using a mixture of hexane/CH_2Cl_2 to yield a pale yellow solid (52%, 3.9 g). ^1H NMR (400 MHz, CD_3CN, δ, ppm): 7.54 (d, *J* = 16 Hz, 9H), 8.02 (m, 6H).

2.3.2. Triphenylcyclopropenium hexafluoroantimonate (2)

Triphenylcyclopropenium chloride (0.90 g, 2.95 mmol) was dissolved in CH_3CN (15 mL). To this solution, sodium hexafluoroantimonate ($NaSbF_6$) (0.72 g, 2.78 mmol) in CH_3CN (15 mL) was added and the mixture stirred at room temperature for 1h. Precipitated NaCl was filtered off. The addition of ether to the filtrate yielded a white solid. Yield: 62% (0.90 g,). M.p.: 319-320 °C. ^1H NMR (300 MHz, CD_3CN, δ, ppm): 7.9 (t, 6H, *J* = 7.6 Hz), 8.1 (t, 3H, *J* = 7.6 Hz), 8.60 (d, 6H, *J* = 7.6 Hz). ^{13}C NMR (75 MHz, CD_3CN, δ, ppm): 119.99, 130.01, 135.85, 138.42, 155.62. MS (ESI): M^- (anion): 234.8, M^+ (cation): 267.1. HRMS (cation): *m/z* calcd. for: $C_{21}H_{15}$ (267.1174); found, 267.1169. Anal. calcd for $C_{21}H_{15}SbF_6$, (503.09): C, 50.13; H 3.01; F, 22.66. Found: C, 50.02; H, 3.03; F, 22.51%.

2.3.3. Triphenylcyclopropenium hydroxytris(pentafluorophenyl)borate (3)

Lithium hydroxytris(pentafluorophenyl)borate was freshly prepared by adding *n*-BuLi (1.6 M in hexane, 1.0 mmol, 0.625 mL) to a solution of $H_2O{\cdot}B(C_6F_5)_3$ (0.50 g, 0.94 mmol) in dry diethyl ether (15 mL) at -78 °C. The mixture was allowed to warm to room temperature over 2h. Removing ether under vacuum resulted in a colorless residue, which was then dissolved in dry and degassed CH_2Cl_2 (25 mL) and then transferred to a solution of triphenylcyclopropenium chloride (0.28 g, 0.94 mmol) in dry and degassed CH_2Cl_2 (25 mL) under argon. A white precipitate (LiCl) was formed and the mixture was stirred overnight at room temperature. The white precipitate was removed by filtration and evaporation of the solvent under vacuum yielded a yellow solid (82%, 0.61 g). M.p.: 61-63 °C. ^1H NMR (400 MHz, CD_3CN, δ ppm): 8.02 (t, 6H, *J* = 7.6 Hz), 8.17 (t, 3H, *J* = 7.6 Hz), 8.70 (d, 6H, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, CD_3CN, δ, ppm), cation: 120.99, 130.65, 134.35, 137.78, 146.97, anion: 135.35, 146.52, 148.98. ^{19}F NMR ($CDCl_3$, $CFCl_3$, δ, ppm): -36.20 (d, 2F, o-F, $J_{F\text{-}F}$ = 23.2 Hz), -160.03 (s, 1F, p-F), -165.24 (t, 2F, m-F, $J_{F\text{-}F}$ = 23.6 Hz). ^{11}B NMR (CD_3CN, $BF_3{\cdot}Et_2O$, δ, ppm): 1.06. MS (ESI): M^- (anion): 528.7, M^+ (cation): 267.0. HRMS (cation): *m/z* calcd. for: $C_{21}H_{15}$ (267.1174), found: 267.1165. HRMS (anion): *m/z* calcd for: $C_{18}HBOF_{15}$ (527.9917) found: 527.9922.

2.4. Polymerization

Commercially available monomers, polyBD®605E, UV9300, UV9315, and UVacure 1500 (Figure 2) were used for initial screening without further purification. Polymerization experiments were conducted in the presence of air at room temperature. UVacure 1500 was mixed with Tone polyol 0301 (75/25% by weight) in glass vials prior to the polymerization. For initial screening, initiator (1 wt.% of the monomer) was mixed with the monomer in glass vials. When necessary, γ-butyrolactone (GBL, 15 wt.% of the monomer or monomer/polyol mixture) was used as a solvent.

Table 1. Initial screening of compound **2** and **3** for epoxy curing (1 weight % of the monomer was used).

Initiator	Monomer	Plasticizer [b]	Time required for polymerization (min) [c]
2	polyBD®605E	-	No polymerization after 2h.
2	polyBD®605E	4	1
3 [d]	polyBD®605E	-	60
2	UVacure 1500 [a]	-	36% polymerization after 2h
2	UVacure 1500 [a]	4	<1
3 [d]	UVacure 1500 [a]	-	<1
2	UV9300	-	No polymerization after 2h
2	UV9300	4	No polymerization after 2h
3 [d]	UV9300	-	5
2	UV9315	-	No polymerization after 2h
2	UV9315	4	No polymerization after 2h
3 [d]	UV9315	-	8

[a] Contains Tone polyol 0301 (25% by weight).

[b] 4 = γ-butyrolactone (15 wt. % of the monomer mixture).

[c] Determined by FT-IR.

[d] Addition of GBL did not noticeably accelerate the polymerization.

For kinetic studies, UVacure 1500/ polyol (10/90% by weight) and 0.1 wt. % initiator was used. Polymerization was monitored by FT-IR on a ZnSe window.

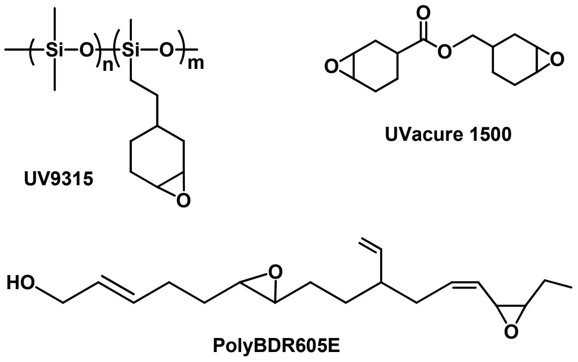

Figure 2. Epoxy monomers used (structure of UV9300 is not available).

3. Results and discussion

The photochemistry of the new hydroxytris(pentafluorophenyl)borate salt, **3**, was studied in dry and oxygen free CH_3CN. Irradiation of compound **3** at 300 nm resulted in formation of hexaphenylbenzene [17,20]. The ^{19}F NMR analysis before irradiation show characteristic ^{19}F NMR spectrum for $HOB(C_6F_5)_3^-$. Upon irradiation of compound **3** the signal corresponding to *para* fluorine of the hydroxytris(pentafluorophenyl)borate anion shifted from -158.56 to -155.75. The spectrum shows the characteristic ^{19}F NMR of adducts of $B(C_6F_5)_3$ such as $H_2O{\cdot}B(C_6F_5)_3$. Destruction of the anion by C_6F_5 group transfer as in *N*-methylisoquinolinium hydroxytris (pentafluorophenyl)borate [11] was not observed**.** In order to test the activities of compound **3** in photopolymerization, the compound (1 wt. % of the monomer) was mixed with UVacure 1500. Immediate polymerization of UVacure 1500 at room temperature was observed. Hence, compound **3** was tested as a room temperature thermal initiator with a series of monomers, and its activity was compared with [TPCP][SbF_6], Table 1.

The initiator, [TPCP] [$HOB(C_6F_5)_3$] (**3**) was soluble in all the monomers, hence direct dispersion of the initiator was possible. [TPCP] [SbF_6] (**2**) was insoluble in the nonpolar monomers, polyBD®605E, UVR9300 and UV9315. It was slightly soluble in UVacure 1500. The direct dispersion of compound **3** in all four monomers initiated polymerization at room temperature (Table 1). Direct dispersion of compound **2** in the polyBD®605E, UV9300, UV9315 did not initiate the polymerization thermally or photochemically because of poor solubility. Polymerization of UVacure 1500/Tone 0301 (75/25% by weight) with compound **2** was slow and only 36% conversion was observed after 2h. When the experiment was repeated by adding GBL (15 wt. % of the monomer), extremely fast, highly exothermic polymerization was observed with both UVacure 1500 and polyBD®605E. Darkening of the polymer was observed with UVacure 1500. The initiator **2** was unsuccessful in polymerization of UV9300 and UV9315 even with GBL because GBL is immiscible with these low polar monomers. In contrast [TPCP][$HOB(C_6F_5)_3$] (**3**) was an effective initiator for thermal polymerization of UV9300 and UV9315 under solvent free conditions (Table 1). Addition of GBL did not noticeably accelerate the polymerization of any of the monomers initiated by compound **3** (Table 1, vide infra).

The kinetics of cationic polymerization of UVacure 1500 by new initiators on a ZnSe window was investigated using FTIR at room temperature. UVacure 1500 was selected as the monomer because disappearance of FTIR epoxy signals can easily be monitored against the carbonyl signal of the monomer. In order to slow down the polymerization rate, initiator concentration was reduced to 0.1 wt. % of the monomer and the monomer/polyol ratio was kept at 90/10% by weight. Intensity of the two bands at 789 and 746 cm^{-1} (due to antisymmetric and symmetric epoxy ring deformation) decreased with time after polymerization was initiated. A new band at 1088 cm^{-1} which is due to C-O-C stretching appeared. The band at 789 cm^{-1} was used to monitor the curing reaction. The carbonyl stretching band of the monomer at 1731 cm^{-1} was used as the internal standard. Initial FT-IR spectrum of the polymerization mixture (before adding the catalyst) was recorded. The polymerization was monitored continuously on a ZnSe window. The percent conversion was calculated using equation 1.

$$\text{Conversion} = [1 - (A_{789}/A_{1731})_t/(A_{789}/A_{1731})_0\,] \times 100\%\ [21] \qquad (1)$$

When compound **2** was employed as initiator only 11% conversion of UVacure 1500 tone (90/10 weight %) was observed in the absence of γ-butyrolactone. The addition of γ-butyrolactone gave more than 50% conversion in less than 2 minutes (Figure 3). Direct dispersion of compound **3** in the monomer mixture initiated the polymerization at room temperature without addition of a solvent. Initially the polymerization was slow in comparison to polymerization with compound **2** with GBL. However, the polymerization rate continued to increase to a higher percent conversion (Figure 3). The same phenomenon was observed when the polymerization was performed in glass vials. Unlike with compound **2**, addition of GBL to the reaction catalyzed by **3** substantially decreased the polymerization rate (with 0.1 wt. % catalyst concentration, Figure 3). However this effect was not observed with 1 wt. % catalyst concentration (Table 1). Results showed that compounds **2** and **3** exhibit excellent activity as room temperature thermal initiators for epoxide polymerization.

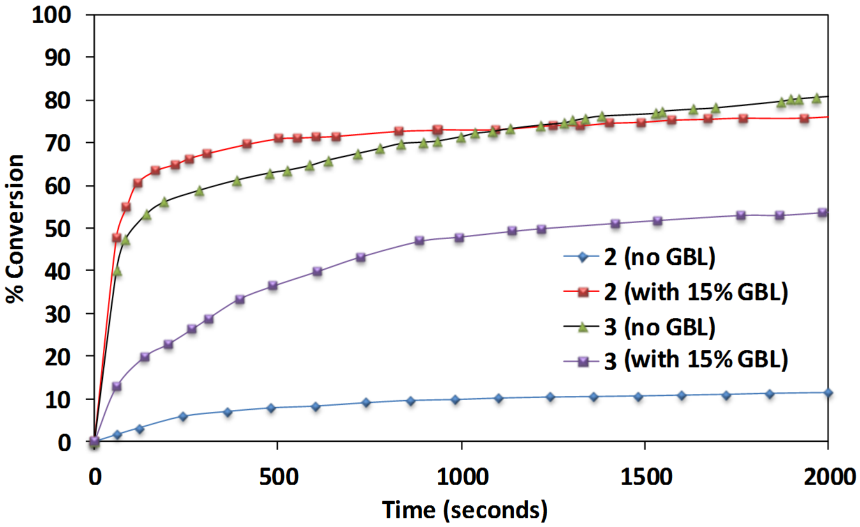

Figure 3. Kinetic profile of polymerization of UVacure 1500/Tone 0301 (90/10 wt. %) with initiators **2** and **3** (0.1 wt. % of the monomer was used).

Initiator compound **3** exhibits excellent solubility in epoxy matrices and showed remarkable activity compared with compound **2** in the absence of GBL; compound **3** does not require cyclohexanone to produce the initiating species as in the case of [TPCP][Ga(C_6F_5)$_4$] [17]. To overcome solubility restrictions, in general, solvents such as γ-butyrolactone are used. However, solvents affect the properties of the polymer and increase the content of volatile organic compounds. Thus, the direct dispersion of the initiator as a solid is an advantage. Once solubility of compound **2** was achieved, compound **2** exhibited the faster initial activity. In most cationic polymerization systems, polymerization ensues exothermically immediately upon mixing the monomer with the initiator. Due to the high reactivity of these systems, it is often difficult to obtain good homogeneous conditions before polymerization starts. Therefore, monitoring the early stages of the polymerization is difficult. The rapid rate of many cationic polymerizations precludes their use as inks, coatings, adhesives, moldings, and other applications. In these applications, a reasonable working life and controlled polymerization rate is required. Consequently, the moderate activity of compound **3** in commercially important monomers such as polyBD®605E, UV9300, UV9315 under solvent free conditions is an advantage for industrial applications.

4. Conclusion

The hydroxytris(pentafluorophenyl)borate anion was identified as a new counter ion for cationic polymerization initiators. When paired with triphenylcyclopropenium cation, it produces compound, triphenylcyclopropenium hydroxytris-(pentafluorophenyl)borate (**3**), which exhibited excellent solubility in commercial monomers to produce industrially important polymers at room temperature, under solvent free conditions.

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