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

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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, SbF6. However, these salts are hydroscopic and insoluble in nonpolar monomers. Unlike SbF6, the highly stable tetraakis(pentafluorophenyl)borate anion, (B(C6F5)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(C6F5)3), which was first reported in 1995 [10] shows unique activity in comparison to B(C6F5)3−. We previously reported a new light induced group transfer reaction in HOB(C6F5)3−[11]. Upon irradiation of N-methylisooquinolininium hydroxytris(pentafluorophenyl)borate, a C6F5 group was transferred from HOB(C6F5)3− to the N-methylisooquinolininium cation [11]. Unlike B(C6F5)3−, the HOB(C6F5)3− is capable of protonating the Zr-Me bond in the Cp2ZrMe2 complex [12]. Various salts of HOB(C6F5)3− have previously been used as a cocatalyst in alkene polymerization [13]. However, HOB(C6F5)3− has not been utilized in cationic polymerization. Due to its unique activities, we decided to explore HOB(C6F5)3− as a counter ion in cationic polymerization initiators and compare its activity to SbF6−.

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(C6F5)3− and SbF6− 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(C6F5)3− [16]. [TPCP][Ga(C6F5)3] requires cyclohexane to form the actual initiating species [16]. In the presence of trace amounts of water, [TPCP][Ga(C6F5)3] also acts as a photoinitiator in polymerization of glycidyl phenyl ether [17].

In this paper, the synthesis of the triphenylcyclopropenium salt paired with hydroxytris(pentafluorophenyl)borate is 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 CDCl3 or CD3CN. Data are reported as follows: multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m = multiplet, br = broad). 13C NMR spectra were recorded on a Varian-400 (100 MHz) NMR spectrometer or a JEOL-300 (75 MHz) spectrometers. 19F NMR spectra and 11B NMR spectra were referenced externally to CFCl3 and BF3.OEt2, respectively. Chemical shifts are reported in parts per million (ppm), in CDCl3 or CD3CN, 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.
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]. H3O.B(C6F5)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 CaSO4 and distilled under vacuum before use. Solvents (Diethyl ether, THF and hexane) were distilled under argon over sodium‐benzophenone prior to use, and otherwise stated. Epoxy monomer, poly BD 2.3.1. Synthesis

2.3. Synthesis

2.3.1. Triphenylcyclopropenium chloride (1)

Diphenylacetylene (4.46 g, 25.20 mmol) was mixed with potassium t-butoxide (7 g, 62.28 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 MgSO4 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/CH2Cl2 to yield a pale yellow solid (52%, 3.9 g). 1H NMR (400 MHz, CD3CN, δ ppm): 7.54 (d, J = 16 Hz, 9H), 8.02 (m, 6H), 8.17 (t, 3H, J = 7.6 Hz). 13C NMR (100 MHz, CD3CN, 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 calc’d for: C15H12 (267.1174); found: 267.1169. Anal. calc’d for C21H15SbF6 (503.09): C, 50.13; H, 3.01; F, 22.66. Found: C, 50.02; H, 3.03; F, 22.51.

2.3.2. Triphenylcyclopropenium hexafluoroantimonate (2)

Triphenylcyclopropenium chloride (0.90 g, 2.95 mmol) was dissolved in CH2CN (15 mL). To this solution, sodium hexafluoroantimonate [NaSbF6] (0.72 g, 2.78 mmol) in CH2CN (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, CD3CN, δ ppm): 7.9 (t, 6H, J = 7.6 Hz), 8.1 (t, 3H, J = 7.6 Hz). 13C NMR (75 MHz, CD3CN, 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 calc’d for: C15H12 (267.1174); found: 267.1169. Anal. calc’d for C21H15SbF6 (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(pentafluoro phenyl)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 H3O.B(C6F5)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 CH2Cl2 (25 mL) and then transferred to a solution of triphenylcyclopropenium chloride (0.28 g, 0.94 mmol) in dry and degassed CH2Cl2 (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, CD3CN, δ ppm): 8.02 (t, 6H, J = 7.6 Hz), 8.17 (t, 3H, J = 7.6 Hz). 13C NMR (100 MHz, CD3CN, 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 calc’d for: C21H15SbF6 (503.09): C, 50.13; H, 3.01; F, 22.66. Found: C, 50.02; H, 3.03; F, 22.51.

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.

Figure 1. Synthesis of triphenylcyclopropenium salts.
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 CH₃CN. Irradiation of compound 3 at 300 nm resulted in formation of hexaphenyldibenzene [17,20]. The ¹⁹F NMR analysis before irradiation show characteristic ¹⁹F NMR spectrum for HOB(C₆F₅)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 ¹⁹F NMR of adducts of B(C₆F₅)₃ such as H₂O·B(C₆F₅)₃. Destruction of the anion by CsF group transfer as in N-methylosoquinolinium 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][HOB(C₆F₅)₃] (Table 1).

The initiator, [TPCP] [HOB(C₆F₅)₃] (3) was soluble in all the monomers, hence direct dispersion of the initiator was possible. [TPCP] [HOB(C₆F₅)₃] (2) was insoluble in the nonpolar monomers, polyBD@605E, UV9300 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(C₆F₅)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 1080 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.

\[
\text{Conversion} = \left[ 1 - \left( \frac{A_{789}}{A_{1731}} \right) / \left( \frac{A_{789}}{A_{1731}} \right) \right] \times 100\% \quad (1)
\]

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.
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(C6F5)3] [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 polyBD8605E, UV9300, UV9315 under solvent free conditions is an advantage for industrial applications.

4. Conclusion

The hydroxytris(pentafluorophenyl)borane 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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