

Design and Synthesis of A New Fluoroepoxy Resin Premonomer

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Abstract

The anti-corrosion performance of materials has always been an indispensable part in the development and application of materials. Epoxy resin is widely used in the field of anti-corrosion due to its excellent anti-corrosion ability, adhesion and mechanical strength. However, with the rapid development of the coating field, the problems of high brittleness and insufficient temperature resistance of epoxy resin are also exposed. In order to improve the shortcomings of conventional epoxy resins that are easy to age and crack, a novel fluoroepoxy monomer was prepared with chlorotrifluoroethylene and 3-chloro-1,2-propanediol as starting materials. which will be used as the prepolymer of high-performance fluoroepoxy resin.

Keywords

Anti-corrosion; Epoxy resin, Fluoroepoxy monomer; Chlorotrifluoroethylene; 3-chloro-1,2-propanediol.

1. INTRODUCTION

Metal and other corrosive materials need to be protected by anti-corrosion technology during use. For materials in different environments, different protection methods can be used to prolong the service life of the material. At present, the anti-corrosion technology of materials mainly includes metal coating, electrochemical protection, dielectric treatment and anti-corrosion coating[1-3], among which the application of anti-corrosion coatings is the most economical and widely used method. As an excellent anti-corrosion material, epoxy resin has the advantages of strong corrosion resistance, good electrical insulation, high adhesion of the formed paint film to the substrate low operating temperature, and simple construction, making it widely used in aerospace, new energy, machinery and other industrial fields and high-tech industries[4-6].

The C-C bonds in PTFE are covered by an all-electronic structure similar to inert gas, which makes PTFE have excellent chemical and thermal stability, and the extremely low surface energy of PTFE material has good hydrophobic and oleophobic properties^{7,8}. The epoxy structure in epoxy resin can be opened by amine, which makes the material have strong compounding ability. After the epoxy structure is introduced into the polytetrafluoroethylene structure, the advantages of the two materials can be combined to obtain a new material with good chemical and thermal stability and excellent bonding performance^[9, 10]. Based on the above consideration, a new type of glycidyl trifluoroethylene prepolymer was designed and synthesized in this article (Figure 1).

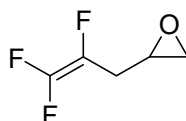


Figure 1. Structure of 2-(2,3,3-Trifluoroallyl)ethylene oxide

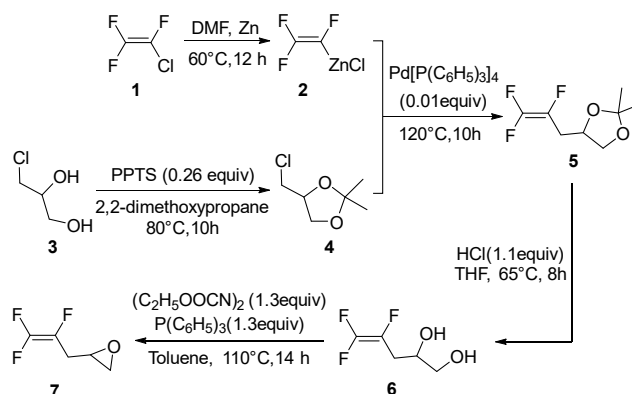


Figure 2. Preparation of fluoroepoxy monomer 7

2. EXPERIMENTAL

Synthesis of (1,2,2-trifluorovinyl)zinc chloride 2

Wash and dry 3.2 g zinc powder with hydrochloric acid (2%), water, acetone and ether, add it into a three-necked flask filled with 120 ml DMF and freeze it with liquid nitrogen. Nitrogen replacement treatment, gradually raise the temperature to 60 °C, slowly use concentrated sulfuric acid dried trifluoroethylene chloride below the DMF liquid level, continue the reaction for 12 h, Filter out excess zinc powder to get filtrate with containing 2.

Synthesis of acetal 3-chloro-1,2-propanediol acetal 4

A solution of 3 (20 mL, 0.24 mol) was added to a three-necked round bottom flask containing 2,2-dimethoxypropane(33 mL, 0.26 mol), then Pyridine-4-toluenesulfonate (5 g, 0.02 mol) was added and the reaction was maintained at 80 °C for 10 h, upon completion the reaction was quenched with brine and extracted with ethyl acetate (3 × 25 mL). The combine organic layer was washed with brine and dried over Na₂SO₄.The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc (4:1) to afford 4 (28.04 g, 77.6% yield). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 4.30~4.26 (m, 1H), 4.05 (dd, *J* = 8.6, 6.4Hz, 1H), 3.72 (dd, *J* = 8.6, 5.6Hz, 1H), 3.65 (ddd, *J* = 19.5, 11.2, 5.6 Hz, 2H), 1.35 (s, 3H), 1.28 (s, 3H). ¹³C NMR (600 MHz, DMSO-*d*₆): δ = 109.57, 75.38, 66.97, 45.78, 27.03, 25.71.

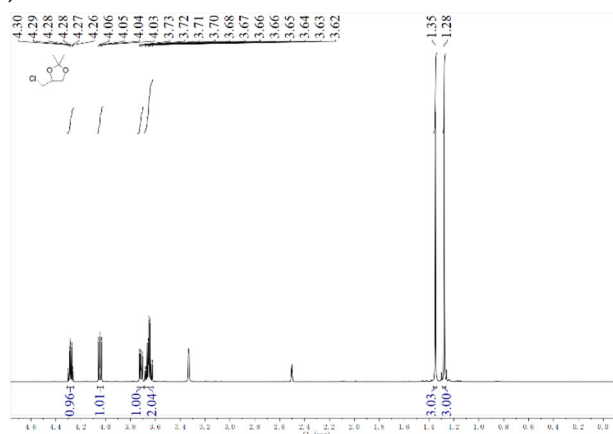


Figure 3. ¹H NMR spectra of compound 4

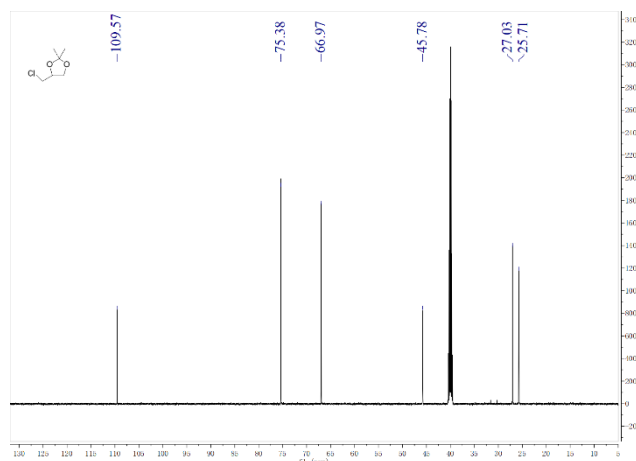


Figure 4. ^{13}C NMR spectra of compound 4

Synthesis of 2,2-dimethyl-4-(2,3,3-trifluoroallyl)-1,3-dioxol **5**

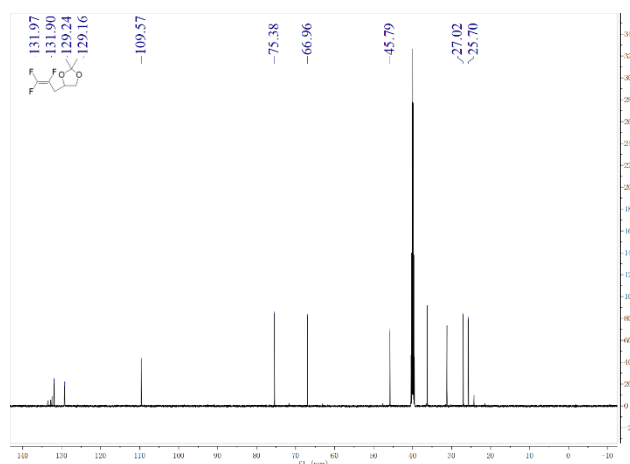


Figure 5. ^1H NMR spectra of compound 5

Since (1,2,2-trifluorovinyl)zinc chloride cannot be stored for a long time, immediately after preparation, filter out excess zinc powder, transfer the remaining filtrate to another three-mouth flask, and freeze in liquid nitrogen. Then, add product **4** (0.4 g, 2.7 mmol) and (20 mg, 0.02 mmol) tetrakis(triphenylphosphino) palladium to the three-necked flask and gradually increase the temperature to 120 °C. The mixture was heated at reflux for 10 h and cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc (6:1) to afford **5** (0.41 g, 78.7% yield). ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 4.30~4.26 (m, 1H), 4.05 (dd, J = 8.6, 6.4Hz, 1H), 3.72 (dd, J = 8.6, 5.6Hz, 1H), 3.65 (ddd, J = 19.5, 11.2, 5.6Hz, 2H), 1.35 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (600 MHz, $\text{DMSO}-d_6$): δ = 131.97, 131.90, 129.24, 129.16, 109.57, 75.38, 66.96, 45.79, 27.02, 25.70. HRMS (ESI) m/z calcd for $\text{C}_8\text{H}_{11}\text{O}_2\text{F}_3$: 196.1463; found: 196.0691 $[\text{M}]^+$.

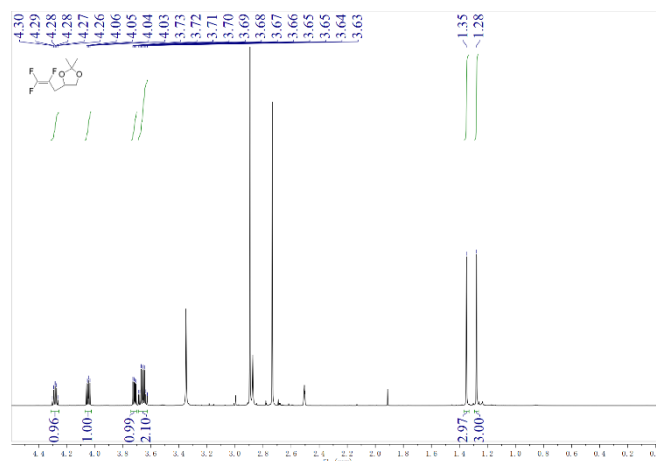


Figure 6. ¹³C NMR spectra of compound 5

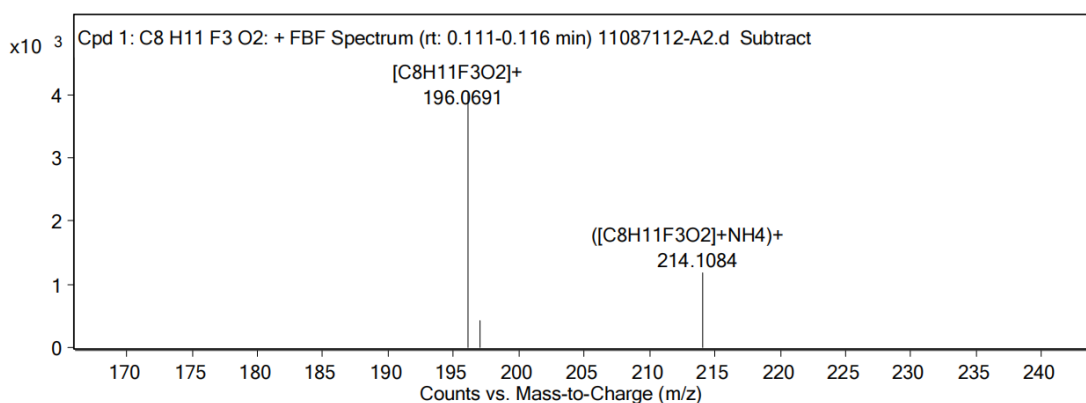


Figure 7. Mass spectra of compound 5

Synthesis of 4,5,5-trifluoropent-4-ene-1,2-diol 6

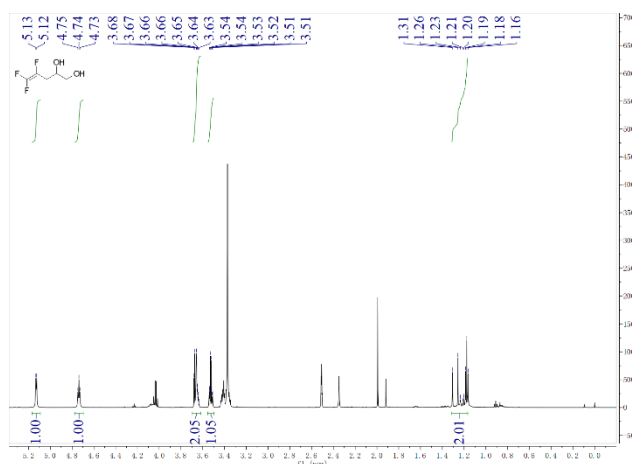


Figure 8. ¹H NMR spectra of compound 6

To a solution of product 5 (0.2 g, 1.0 mmol) was placed in a three-necked flask containing 20 ml of tetrahydrofuran, heated to 65 °C, and 2 ml of 1 mol/L hydrochloric acid was added continuously and slowly through a constant pressure drip funnel. After dropwise addition, the reactants were maintained at 65 °C for 8 h, saturated sodium bicarbonate was added and quenched, and the reaction mixture was extracted with ethyl acetate (3 × 25 mL). The combine organic layer was washed with brine and dried over Na₂SO₄.The solvent was removed under

reduced pressure, and the residue was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc (3:1) to afford **6** (0.12 g, 75.4% yield). ^1H NMR (600 MHz, $\text{DMSO-}d_6$): δ = 5.12 (d, J = 5.2 Hz, 1H), 4.74 (t, J = 11.3 Hz, 1H), 3.68~3.60 (m, 2H), 3.55~3.50 (m, 1H), 1.16~1.31 (m, 2H). ^{13}C NMR (600 MHz, $\text{DMSO-}d_6$): δ = 131.98, 131.91, 129.27, 129.19, 71.72, 63.10, 47.65. HRMS (ESI) m/z calcd for $\text{C}_5\text{H}_7\text{O}_2\text{F}_3$: 156.0893; found: 157.045 $[\text{M}+\text{H}]^+$.

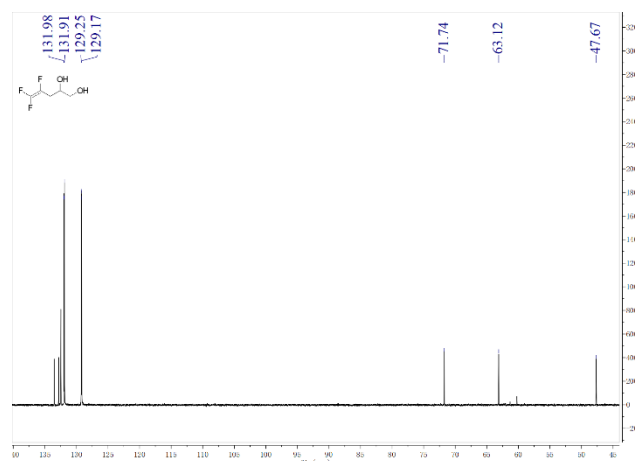


Figure 9. ^{13}C NMR spectra of compound **6**

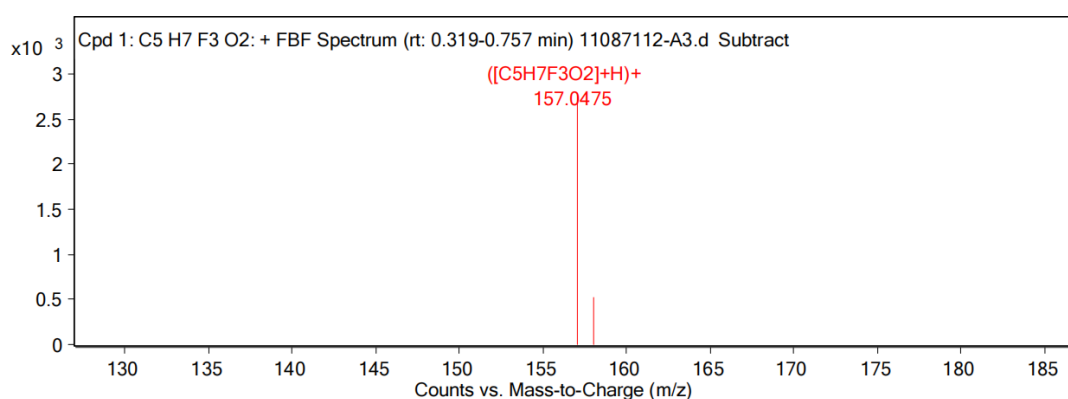


Figure 10. Mass spectra of compound **6**

Synthesis of 2-(2,3,3-trifluoroallyl) ethylene oxide **7**

A solution of product **6** (0.08 g, 0.5 mmol), triphenylphosphine (0.18 g, 0.7 mmol) and diethyl azodicarboxylate (0.1 mL, 0.7 mmol) was added to 20 ml of toluene, the reactants were maintained at 110 °C for 8 h, quenched with saturated saline, and the reaction mixture was extracted with ethyl acetate (3 × 25 mL). The combined organic layer was washed with saturated saline, dried with Na_2SO_4 , the solvent was removed under reduced pressure, and the residue was eluted with petroleum ether/EtOAc (2:1) and the silica gel was quickly purified by column chromatography to obtain **7** (0.07 g, yield 98.9%). ^1H NMR (600 MHz, $\text{DMSO-}d_6$): δ : 3.89 (dd, J = 11.7, 3.8 Hz, 1H), 3.54 (dd, J = 11.8, 7.0 Hz, 1H), 3.23 (ddd, J = 12.2, 3.9, 2.5 Hz, 1H), 2.85 (dd, J = 5.0, 4.1 Hz, 1H), 2.70 (dd, J = 5.1, 2.5 Hz, 1H). ^{13}C NMR (600 MHz, $\text{DMSO-}d_6$): δ = 131.98, 131.92, 129.26, 129.18, 78.22, 63.36 cm^{-1} .

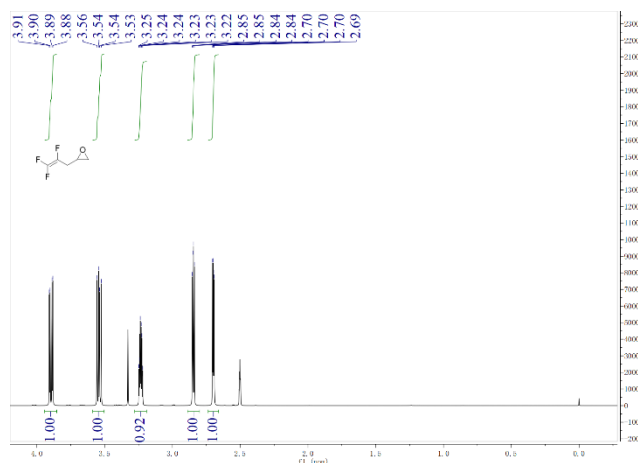


Figure 11. ^1H NMR spectra of compound 7

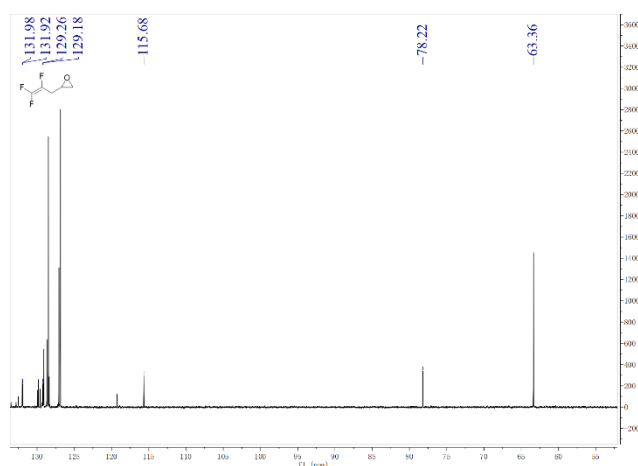


Figure 12. ^{13}C NMR spectra of compound 7

3. CONCLUSION

The fluoroepoxy monomer was synthesized through five-step reaction with 3-chloro-1,2-propanediol and trifluoroethylene as starting materials in Figure 2. Firstly, the dihydroxy structure in 3-chloro-1,2-propanediol 1 was protected with acetylidene in the presence of pyridinium 4-toluenesulfonate to synthesize 3-chloro-1,2-propanediol acetal 2[11, 12]. Then it was conjugated with the prepared zinc trifluorochloride Grignard reagent to generate 2,2-dimethyl-4-(2,3,3-trifluoroallyl)-1,3-dioxolane 5, which subsequently released the protected dihydroxy structure under acidic conditions to give compound 6. Finally, the epoxidation of the *o*-dihydroxyl groups in 6 afforded the final fluorine-containing epoxy monomer 7[13].

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