

9, 9'-비스[4-(2'-하이드록시-3'-아크릴로일옥시프로폭시) 페닐]플루오렌의 원자효율적 합성

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Atom-efficient Preparation of 9, 9'-Bis[4-(2'-hydroxy-3'-acryloyloxypropoxy)phenyl]fluorene

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요 약

플루오렌 구조를 가진 다양한 아크릴계 에폭시 고분자화합물 합성의 전구물질인 9, 9'-비스[4-(2'-하이드록시-3'-아크릴로일옥시프로폭시)페닐]플루오렌 (3)에 대한 원자 효율적 (atom-efficient) 제조방법을 연구하였다. 사차 암모늄 또는 인산염을 촉매를 사용하여 9, 9'-비스[4-(글라이시딜옥시)페닐]플루오렌 (1)을 아크릴산과 개환 에스터화의 효율적 반응을 통하여 9, 9'-비스[4-(2'-하이드록시-3'-아크릴로일옥시프로폭시)페닐]플루오렌 (3)을 높은 수율로 얻을 수 있었다. 알킬 사차염의 종류와 반응조건이 반응에 미치는 영향에 대해 조사한 결과, 촉매의 종류가 반응에 큰 영향을 미치는 것으로 나타났다. 브롬화사부틸인 촉매(3 mol%) 존재 하에 플로레닐에폭사이드를 아크릴산과 110 °C에서 반응시켰을 때 원하는 생성물을 90% 수율로 얻을 수 있었다. 이 반응은 반응물질 사용량과 화학적 폐기물의 생성량을 최소화한 청정반응이다.

주제어 : 원자효율적반응, 플루오렌, 9, 9'-비스[4-(글라이시딜옥시)페닐]플루오렌, 녹색화학, 개환 에스터화반응, 사알킬화염 촉매

Abstract : Atom-efficient preparation of 9, 9'-bis[4-(2'-hydroxy-3'-acryloyloxypropoxy) phenyl]fluorene (3), the extensively used building block for fluorene-containing acrylic epoxy polymers has been described. The epoxide ring opening esterification of 9, 9-bis[4-(glycidyl)oxy]phenyl]fluorene (1) with acrylic acid was catalyzed by some onium salts such as quaternary ammonium and phosphonium salts. While the coupling reactions depend greatly on the kind of the onium salts, the reaction of 9, 9-bis[4-(glycidyl)oxy]phenyl]fluorene (1) with acrylic acid proceed most efficiently in the presence of a catalytic amount of tetrabutylphosphonium bromide at 110 °C with 90% yield. This reaction is a cleaner reaction that minimizes the use of reactants and the production of chemical wastes.

Keywords : Atom-efficient reaction, Fluorene, 9, 9-bis[4-(glycidyl)oxy]phenyl]fluorene, Green chemistry, Ring-opening esterification, Tetraalkyl onium salt

1. Introduction

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Green chemistry has attracted much attention in organic che-

mistry[1-4]. Major goal in this area is to maximize the efficient use of raw materials and simultaneously to minimize waste. In this context, conversion of conventional organic processes into the highly atom-efficient protocol with good selectivity is the most desirable. Fluorene-containing polymers have attracted research interests due to their excellent properties such as good heat resistance, high refractive index, high transparency and low linear expansion coefficient. The higher rigidity of fluorene skeleton in the chain backbone of four phenyl rings connected to a quaternary carbon is considered to be responsible for their desirable properties[5-8].

We have reported an example of a green reaction in the area of fluorene-containing structures by showing the fluorenyl epoxide can be converted into the cyclic carbonate (2) by reaction with carbon dioxide in a highly atom-efficient manner[9]. We have noticed such processes catalyzed by quaternary onium salts such as tetraalkylammonium and phosphonium halides can proceed in an efficient, clean and by-product-free manner. As another example of the atom-efficient transformation in the area of fluorene-containing compounds, we studied a reaction of the glycidyl ether of 9, 9'-bis(4-hydroxyphenyl)fluorene (1) into 9, 9'-bis[4-(2'-hydroxy-3'-acryloyloxypropoxy) phenyl]fluorene (3), a useful precursor for preparing many fluorene-containing polymers[10-13] as shown in Figure 1.

While the use of epoxy resins of acrylate compound containing 9, 9'-bis(4-hydroxyphenyl) fluorene has been increasing nowadays, the detailed synthetic procedures for preparing such compounds

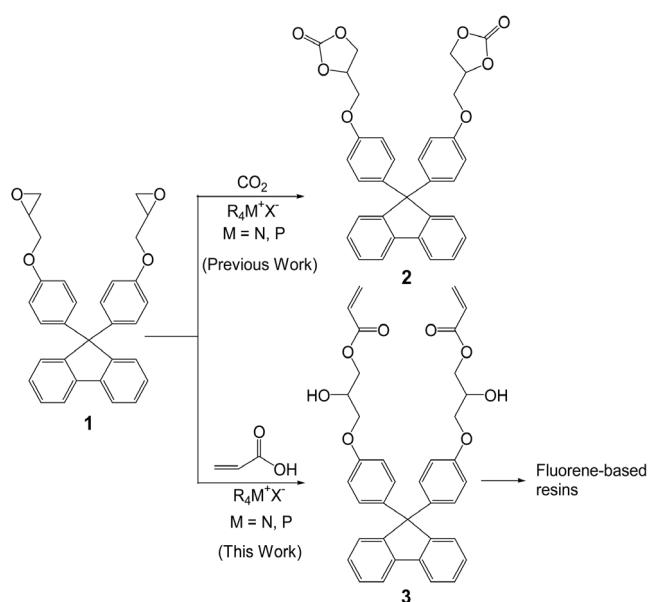


Figure 1. Synthetic route for the preparation of 9,9'-bis[4-(2'-hydroxy-3'-acryloyloxypropoxy) phenyl] fluorene (3) and 9,9'-Bis(4-(2-oxo-[1,3]dioxolanyl methoxy)phenyl)fluorene (2) starting from 9,9'-bis[4-(glycidyloxy)phenyl]fluorene (1).

are surprisingly limited except for a few examples. Compound 3 can be synthesized in two steps by the reaction between 9, 9'-bis(4-hydroxyphenyl)fluorene, epichlorohydrin and then acrylic acid. The procedure consists of two steps; the reaction of 9, 9'-bis(4-hydroxyphenyl)fluorene and epichlorohydrin to produce 9, 9'-bis[4-(glycidyloxy)phenyl]fluorene (1) and the following coupling of 9, 9'-bis[4-(glycidyloxy)phenyl]fluorene (3) with acrylic acid. In the course of preparing photocurable resins, we needed 9, 9'-bis[4-(2'-hydroxy-3'-acryloyloxypropoxy) phenyl]fluorene (3) in a quantity, but the previous procedures was not satisfactory to us to prepare 3, in terms of the chemical yield, handling and isolating methods in a large scale. We have found the coupling of 9, 9'-bis[4-(glycidyloxy)phenyl]fluorene (2) with acrylic acid proceed efficiently when catalyzed by quaternary onium salts. Herein, we report our efforts to improve the preparation of 3 starting from 9, 9'-bis(4-hydroxyphenyl) fluorene.

2. Experimental

9, 9'-Bis(4-hydroxyphenyl)fluorene (97%), was purchased from Ferraniait (Italy) epichlorohydrin and anhydrous magnesium sulfate were obtained from Daejung Chemicals and Metal Co. Ltd. (Korea) Reagent Co. Ltd. (China). Other Chemicals (analytical reagent, unless otherwise stated) were purchased from Aldrich Chemical Co. (U.S.A.) and used without further purification.

2.1. Synthesis of 9, 9'-Bis(4-oxiranylmethoxyphenyl)fluorene (1)

9, 9'-bis(4-oxiranylmethoxyphenyl)fluorene was prepared by the reaction of 9, 9'-bis(4-hydroxyphenyl) fluorene with epichlorohydrin using known literature procedures[9,15].

2.2. Synthesis of 9, 9'-Bis[4-(2'-hydroxy-3'-acryloyloxypropoxy)phenyl]fluorene (3)

A typical experimental procedure for the coupling reaction of 9, 9'-bis(4-oxiranylmethoxyphenyl)fluorene with acrylic acid is as follows. The solution of 9, 9'-bis(4-oxiranylmethoxyphenyl) fluorene (354.8 g, 774.7 mmol), acrylic acid (118 mL, 1705 mmol), tert-butyl-4-methylphenol (342 mg, 1.55 mmol), and tetrabutylphosphonium bromide (7.89 g, 23.2 mmol) in 1-methoxy-2-propyl-acetate (PGMEA, 500 mL) was heated at 110 °C for 12 h. The cooled mixture was concentrated under reduced pressure and the residual mixture was extracted twice with dichloromethane (5 L). The separated organic phase was washed with saturated sodium bicarbonate (2 L), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residual oil was purified by flash column chromatography on silica gel (elution with 33% ethyl acetate in hexane) to give 3 as a white hygroscopic powder (419.3 g, 90.1%).

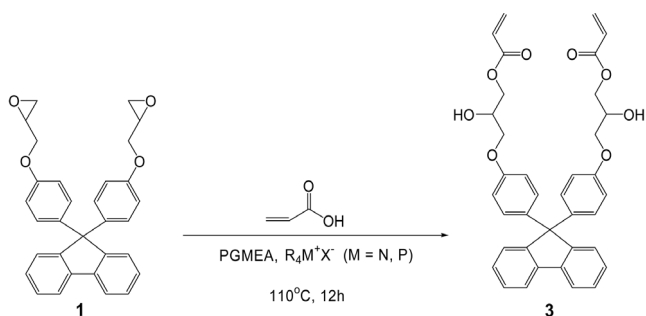
Table 1. Spectral data of 9, 9'-bis[4-(2'-hydroxy-3'-acryloyloxypropoxy)phenyl] fluorene (3)

¹ H NMR (300 MHz, CDCl ₃)	δ 2.52 (d, J = 5.1 Hz, 2 H), 3.96 - 4.35 (series of m, 10 H), 5.87(d, J = 10.5 Hz, 2 H), 6.14 (m, 2 H), 6.76(d, J = 8.4 Hz, 4 H), 7.10 (d, J = 8.4 Hz, 4 H), 7.24-7.37 (series of m, 8 H), 7.75(d, J = 7.2 Hz, 2 H).
¹³ C NMR (75 MHz, CDCl ₃)	ppm 166.29, 157.05, 151.57, 139.94, 138.82, 131.72, 129.25, 127.84, 127.76, 127.45, 125.95, 120.21, 114.19, 68.56, 68.51, 65.41, 64.13.
IR (KBr, pellet)	cm ⁻¹ 3413, 2952, 1717, 1635.
HRMS	calcd for C ₃₇ H ₃₄ O ₈ m/z (M ⁺) 606.2244, found 606.2258.
Elemental analysis	calcd for C ₃₇ H ₃₄ O ₈ : C, 73.25; H, 5.65, found: C, 72.94; H, 5.52.

3. Results and Discussion

The procedure for the ring-opening esterification of 9, 9'-bis[4-(glycidyloxy)phenyl]fluorene (1) with methacrylic acid to form the methacrylic ester using N,N-dimethylbenzylamine catalyst was described previously[15]. However, the chemical yield was not satisfactory and the purification of the product with a moderate yield (ca. 60%) was tedious (Table 2, entry 1), we needed to improve this process further. We have reported earlier quaternary onium salts such as tetraalkylammonium and phosphonium halides can catalyze the ring-opening addition of styrene oxide with carbon dioxide. We found quaternary onium salts again accelerate the ring-opening of 9, 9'-bis[4-(glycidyloxy)phenyl]fluorene (1) with acrylic acid to produce the desired acrylic ester using quaternary onium salts such as tetraalkylammonium and phosphonium halides proceeds efficiently(Figure 2).

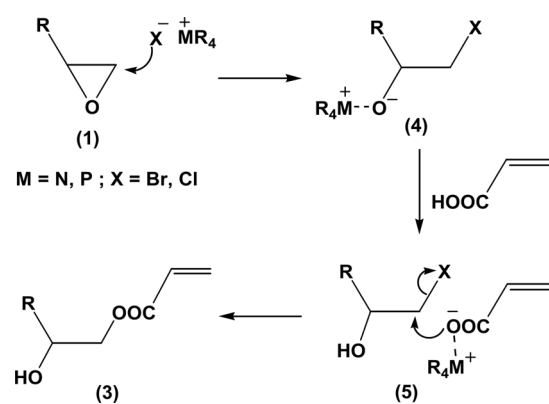
The reactions depend quite on the kind of the onium salts. Table 1 shows the results of the experiments performed for the coupling reaction of 9, 9'-bis[4-(glycidyloxy)phenyl]fluorene (1) with acrylic acid in the presence of catalytic amounts of several quaternary ammonium or phosphonium salts (3 mol%). The reaction catalyzed by tetraalkylphosphonium salts (entry 4-7) gave a higher yield than tetraalkylammonium salts (entry 2-3). For tetrabutylphosphonium bromide-catalyzed reaction, the optimized yield (90%) was achieved (entry 10). Table 1 shows our procedure was superior than the previous method[15] in terms of yield

**Figure 2.** Preparation of 9, 9'-bis[4-(2'-hydroxy-3'-acryloyloxypropoxy)phenyl] fluorene (3) from 9, 9'-bis[4-(glycidyloxy)phenyl]fluorene (1) and acrylic acid.

and the used amount of the raw material (acrylic acid). Our method requires only 2.2 eq. of acrylic acid while the previously reported method uses more than 3 times (6.7 eq.). Also, our method shows much higher yields (74-90%) compared to 62% of the previously reported method. This means that our method uses much less organic material but produces the desired product up to 45% higher yield, requiring less energy and utilities to make the same amount of the product. Therefore, our method is a greener or cleaner method in producing 9, 9'-bis[4-(2'-hydroxy-3'-acryloyloxypropoxy)phenyl]fluorene (3) than the previously reported method.

Table 2. Effect of catalysts and reaction conditions on the coupling reaction of 9, 9'-bis[4-(glycidyloxy)phenyl]fluorene (2) with acrylic acid

entry	Catalyst	Used acrylic acid (eq.)	Yield (%)
1	N,N-dimethylbenzylamine	6.7 eq. (ref. 15)	62
2	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)	2.2 eq. (this work)	74
3	C ₆ H ₅ CH ₂ N(Br)(C ₂ H ₅) ₃		73
4	CH ₃ CH ₂ P(Br)(C ₆ H ₅) ₃		81
5	CH ₃ P(Br)(C ₆ H ₅) ₃		84
6	C ₆ H ₅ CH ₂ P(Br)(C ₆ H ₅) ₃		86
7	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ P(Br)		90

**Figure 3.** Plausible reaction mechanism for the ring-opening esterification of 9, 9'-bis[4-(glycidyloxy)phenyl]fluorene (1) with acrylic acid in the presence of quaternary onium salts.

The mechanistic role of the tetraalkylonium halide in the epoxide ring opening process is probably common with the ring-opening addition of styrene oxide with carbon dioxide[17] the epoxide ring is coordinated to the onium ion, and the resulting coordinated epoxide ring (4) is opened by the halide ion to form a haloalkoxy species (5), and nucleophilic attack of the acrylate on haloalkoxy species leads to the product (3)(Figure 3).

4. Conclusions

An atom-efficient preparation of compound 3, the extensively used building block for fluorene-containing polymers has been described. It was synthesized in two steps glycidyl ether formation of 9, 9-bis(4-hydroxyphenyl) fluorene by reaction with epichlorohydrin and the following epoxide ring opening esterification of glycidyl ether of 9, 9-bis(4-hydroxyphenyl) fluorene (1) with acrylic acid. The epoxide ring opening esterification of 1 with acrylic acid was catalyzed by some onium salts such as quaternary ammonium and phosphonium salts. The coupling reactions depend greatly on the kind of the onium salts and the coupling reactions with catalytic amount of tetrabutylphosphonium bromide at 110 °C gave the best result. The mechanistic role of the quaternary onium salts in this epoxide ring opening esterification involving a haloalkoxy species was described.

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