

Synthesis of Difuran Derivatives by Photolytic Coupling for Use as Biorenewable Monomers

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Abstract: Difuran derivatives were synthesized using 2-furfural, furan, furfuryl alcohol, and 2-(2-furyl)-1,3-dioxolane by photochemical coupling with 5-bromo-2-furfural in a flow-through system with an anionic exchange column. The reactions were performed with various UV light sources. The coupling of 5-bromo-2-furfural and furan produced the highest yields. [2,2'-Bifuran]-5-carboxaldehyde will be used to synthesize a methacrylated monomer which can be used to cross-link photopolymerized polymers by Diels-Alder reaction. The physical properties of these polymers will be analyzed.

1. Introduction

Increasing crude oil prices and instability throughout the oil industry have led to greater interest in high-performance polymers synthesized from biorenewable resources, such as lactic acid or furfural.^{1,2} Furfural, which is a byproduct of corn processing, and its derivatives show potential for use as active pharmaceutical reagents,^{3,4} organic photodiodes,⁵ and ferroelectric liquid crystals.⁶ Since furfural is available in large quantities, it is also a compelling starting block for synthesis of monomers that could lead to high performance materials, with structures similar to those based on other aromatic compounds, such as toluene diisocyanate, but biodegradable.⁷

5,5'-Diformyl-2,2'-bifuran is one such promising monomeric building block. Its photochemical synthesis from 5-bromo-2-furfural and 2-furfural has been described using an anionic exchange resin, Reillex[®] 402, to remove acid as product formed (see Scheme 1).⁸ With this scheme, high yields of 87% were reported based on an equimolar ratio of the reactants and a quantity of the ion exchange resin that would only absorb a fraction of the HBr produced during the reaction. However, these high yields were not reproducible due to absorption of the UV light by the reactant and acid-catalyzed polymerization reactions.

An improved technique to synthesize bifuran compounds from furan and 2-(2-furyl)-1,3-dioxolane by photochemical coupling with 5-bromo-2-furfural has been developed that utilizes a flow-through system (see Figure 1) and anionic exchange resin quantities with exchange capacities approximately 100 times more than the amount of acid produced. Selection of the UV light for the reaction depended on the UV absorbance of the reactants. The novel compounds synthesized will be analyzed. The physical properties of polymers from these monomers will be analyzed using dynamic mechanical analysis (DMA) and the cantilever-bend method to determine relative shrinkage stress.⁹

2. Experimental

2.1 Materials

Furan and 2-furfural (Aldrich Chemical Co.) were distilled under reduced pressure to remove inhibitor and impurities, while 5-bromo-2-furfural (97%, Aldrich) was used as received. Ion exchange resins Amberlyst 21A (A-21A) and Amberlyst 15 (A-15) were activated according to manufacturer's instructions (Aldrich). Acetonitrile (99%), ethylene glycol (99%), chloroform (99%), dichloromethane (99%), p-toluene sulfonic acid (98%), and toluene (99%) (Fisher Scientific Co.) were dried over molecular sieves. Bismaleimide (Alfa-Aesar), furfural methacrylate, 2-hydroxyethyl methacrylate, (1-methylethylidene) bis [4,1-phenyleneoxy (2-hydroxy-3,1-propanediyl)] bismethacrylate (Bis-GMA), camphorquinone (CQ), and ethyl 4-dimethyl amino benzoate (EDMAB) were purchased from Aldrich and used as received.

2.2 Synthesis and Characterization

Product and reactant analysis. UV/Vis spectroscopy was performed using a Photodiode Array spectrophotometer HP 8453, Agilent Technologies, Inc. Santa Clara, CA, USA) over 220-400 nm. Reactants were mixed in acetonitrile and diluted to appropriate concentrations for spectral acquisition.

Products were analyzed by gas chromatography (GCMS-QP5000, Shimadzu Scientific Instruments, Columbia, MD, USA). Helium was used as the carrier gas at a flow rate of 1.1 m³/min. The GC was operated in split mode with an AOC-20i autosampler (Shimadzu, Scientific Instruments, Columbia, MD, USA). Chromatographic separations were performed on a 30-m x 0.25-mm, 0.25- μ m d_f

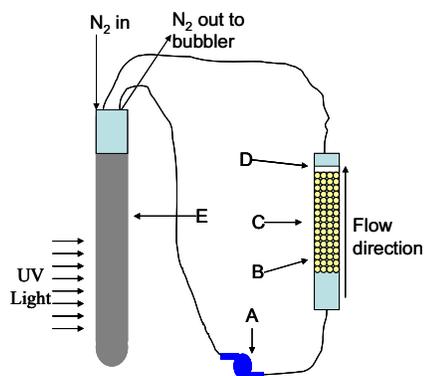


Figure 1. Schematic of microscale reaction system: (A) peristaltic pump, (B) ion exchange column, (C) A-21A resin, (D) glass frit, (E) quartz test tube with rubber stopper.

XTI-5 column (Restek, Bellefonte, PA) with an electron ionization (EI) source. The GC/MS program used to monitor progress on monomer synthesis reactions was as follows: 80°C for 2 min at 5°C/min, to 160°C or 280°C (depending on the molecule being analyzed), and held at the final temperature for 2 min. The injection port and source were maintained at 300°C. Full-scan EI data were collected in all experiments at the following conditions: ionization energy = 70 eV, mass range = 20–500 amu, and scan time = 2 scan/s. All analyses were performed setting the electron multiplier voltage at 1.5 kV.

¹H NMR spectra of the monomers and monomer building blocks were obtained on a 400 MHz NMR Spectrometer (Bruker DRX-400, Bruker Biospin Corp., Billerica, MA, USA) using 5-mm OD

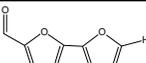
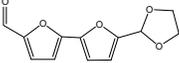
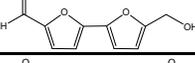
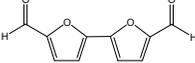
tubes. Sample concentrations were ~10% (w/v) in acetone-d₆ or chloroform containing 0.1% v/v tetramethyl silane, TMS.

Synthesis of 2-(2-furyl)-1,3-dioxolane. A 1000-mL round bottom flask, dean stark trap, and stir bar were dried at 130°C for 12 h, fitted with rubber septa, and cooled under a flow of dry nitrogen. Toluene (700 mL), furfural (67.93 g), ethylene glycol (86.89 g), and p-toluene sulfonic acid (0.25 g) were added to the flask under dry nitrogen purge. The system was refluxed for 24 h, and sodium bicarbonate (0.12 g) was added to neutralize the acid catalyst. The mixture was then filtered through sodium bicarbonate, and the solvent was removed under reduced pressure. Once the solvent evaporated, the residue was distilled *in vacuo* to yield 2-(2-furyl)-1,3-dioxolane as a colorless liquid (49.61 g, 50%). bp 89-90°C/15 mm (89°C/15mm¹⁰).

Preparation of A-21A ion exchange column. Wet A-21A (12 g) was placed in a column with a 1-cm ID. Acetone was pumped through the column to remove water and residual organics from processing, and the column was dried at 100°C under vacuum for 12 h to remove traces of water. The column was then sealed at one end with a rubber stopper and filled with acetonitrile. The column and acetonitrile were degassed under sonication and light vacuum.

Synthesis of [2,2'-bifuran]-5-carboxaldehyde (1, Table 1). Acetonitrile (50-mL), 5-bromo-2-furfural (0.100 g, 5.71×10⁻⁴ mol), and furan (9.99×10⁻⁴ mol) were added to a 60-mL quartz test tube equipped with a rubber stopper and magnetic stir bar. The solution was pumped through a continuous loop system, which included the ion exchange column (see Figure 1). Solvent lost to the tubing in the flow system was replaced in the test tube with degassed acetonitrile (≈20 mL) via syringe within the first few minutes of startup, and the system was allowed to equilibrate and pumped for 30 min. The system was kept under nitrogen purge for the duration of the experiment. An 8-W, 254-nm germicidal lamp (Phillips TUV 8-W Hg lamp) was used to initiate the reaction. The reaction was monitored with GC/MS to determine when the reaction was complete. The solvent was removed under vacuum, leaving a light yellow oil. The oil was dissolved in a minimum volume of pentane and crystallized at -20°C, forming yellow crystals (60 mg) from pentane.¹¹ ¹H NMR: δ=9.66 (1H, s, CHO) δ=7.78 (1H, d, J=1.5 Hz), δ=7.54 (1H, d, J=3.5 Hz), δ=7.0 (1H, d, J=3.5 Hz) δ=6.91 (1H, d, J=3.5 Hz), δ=6.68 (1H, d, J=3.5 Hz); GC/MS: m/z = 105.03 (M⁺, C₇H₅O, 100%), 162.02 (54%, C₉H₅O₃).

Table 1. Synthesis of potential monomers from the photolytic coupling method.

| Chemical Name | Structure | Number |
|---|---|--------|
| [2,2'-bifuran]-5-carboxaldehyde |  | 1 |
| 1,3-Dioxolane-5-carboxaldehyde-[2,2'-bifuran] |  | 2 |
| [2,2'-bifuran]-5-carboxaldehyde-5-2-furancarbinol |  | 3 |
| [2,2'-bifuran]-5,5'dicarboxaldehyde |  | 4 |

Synthesis of other difuran derivatives. 1,3-Dioxolane-5-carboxaldehyde-[2,2'-bifuran] (2, Table 1), [2,2'-bifuran]-5-carboxaldehyde-5-2-furancarbinol (3, Table 1), [2,2'-bifuran]-5,5'dicarboxaldehyde (4, Table 1) were synthesized according to the same procedure as [2,2'-bifuran]-5-carboxaldehyde. Separations have not yet been fully realized, and yields are based on GC/MS chromatographs. GC/MS:

2 with m/z 234.15 (M^+ , 100%) with a retention time of 28.8 min, **3** with m/z 190.16 (M^+ , 100%) with a retention time of 23.04 min, and **4** with m/z of 192.25 (M^+ , 100%) with a retention time of 24.29 min.

Synthesis of Diels-Alder product (DAI). Furfuryl methacrylate (5.98 g), N,N' -bismaleimido-4,4'-diphenylmethane (3.368 g), hydroquinone (1 g), and chloroform (100 mL) were added to a 250-mL round bottom flask and heated to reflux (65°C) under nitrogen purge for 48 h. The chloroform was removed *in vacuo*, and the reaction product was precipitated in diethyl ether (50 mL). The filtrate was rinsed with excess ether to remove residual starting materials. The product was analyzed with NMR, and the structure was confirmed (see Figure 2 for Proton NMR Assignments). 1H NMR: H_g and H_h (8 H, m $\delta=7.30-7.00$), H_e (4 H, m $\delta=6.56$), H_c (2 H, d, $\delta=6.16$), H_b (2 H, d, $\delta=5.61$), H_d (4 H, d's, $\delta=5.08, 4.95, 4.75, 4.61$), H_i (2 H, s $\delta=4.03$), H_j (endo H, dd, $\delta=3.84$, d, $\delta=3.57$), H_j (exo H, dd, $\delta=3.11$), H_a (6 H, d, $\delta=1.96$)

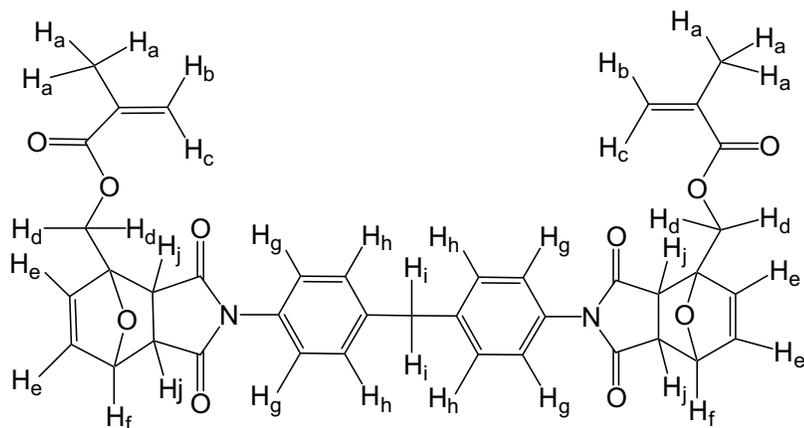


Figure 2. Diels-Alder product from furfuryl methacrylate and N,N' -bismaleimido-4,4'-diphenylmethane.

Synthesis with HEMA/DAI and HEMA/Bis-GMA photopolymerized co-polymers. Monomers were mixed in 5-mL vials according to Table 2. After mixing in vial, the samples were mixed by hand, and then sonicated for 20 min. Polymerization will be discussed in the forthcoming sections.

Table 2. Formulations for Bis-GMA/HEMA and Diels-Alder product/HEMA

| Sample | Bis-GMA wt% (mol%) | D-A Product wt% (mol%) | HEMA wt% (mol %) | CQ (wt%) | EDMAB (wt%) |
|--------|-----------------------|---------------------------|---------------------|-------------|----------------|
| B1 | 65(32) | 0 | 35 (68) | 1 | 1 |
| DA1 | 0 | 71 (32) | 29 (68) | 1 | 1 |
| DA2 | 0 | 55 (19) | 45 (81) | 1 | 1 |
| DA3 | 0 | 40 (11) | 60 (89) | 1 | 1 |

2.3 Physical Property Testing

Dynamic mechanical analysis. Thermal and mechanical transitions were recorded with a TA Q 800 (TA Instruments, New Castle, Delaware) by heating from 25-200°C at 3.0 °C/min at a frequency of 1 Hz with 0.1% strain applied throughout the program. The dual cantilever clamp was used with samples made from resin compositions listed above. The rectangular bars (30 mm x 10 mm x 2 mm) were made

by irradiating 1.5 g of Bis-GMA/HEMA or DA1/HEMA samples for 30 min with a 200-W Hg-Xe lamp (Oriental Instruments, Stratford, CT, USA) with a water filter attached to remove infrared wavelengths.

Shrinkage stress testing. Brass cantilever method was used to measure shrinkage stress.¹² Brass cantilevers (5 cm x 12.7 mm x 0.051 mm) were fixed in the cantilever setup for measurement of shrinkage stress (Figure 3), and the initial curvature was noted. Then, 15 μ L of the formulations shown in Table 2 were applied to brass cantilevers and irradiated for 10 min each with a 1000 W Hg/Xe arc lamp (Newport Corporation, Irvine, CA), equipped with a mechanical shutter and a water filter to remove infrared wavelengths. After irradiation, the curvature of the cantilever was measured, and the original curvature was subtracted to determine the shrinkage stress.

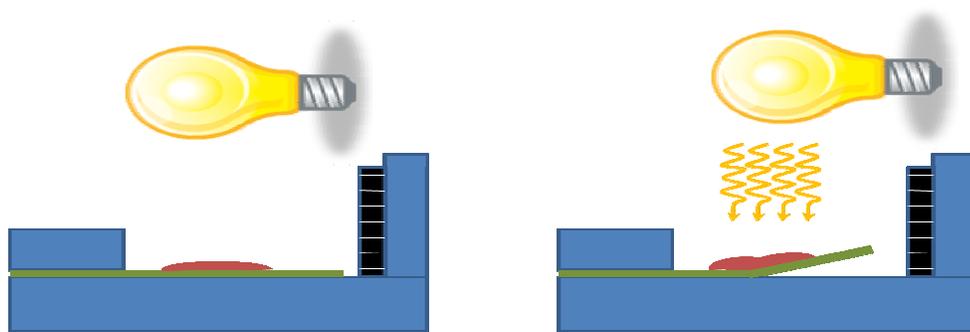


Figure 3. Cantilever shrinkage stress apparatus before polymerization (left) and after polymerization (right).

3. Results and Discussion

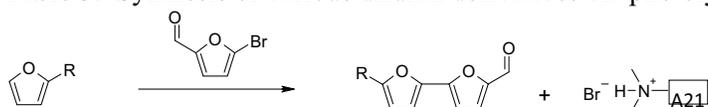
3.1 Synthesis of difuran derivatives

The synthesis of 5,5'-diformyl-2,2'-bifuran (**1F**, Table 2), when attempted according to the methods in Ref. 8, did not reach high yields, and polymeric resins were produced through acid-catalyzed polymerization reactions. Therefore, the amount of anionic exchange resin was increased to 100 times the amount of HBr formed during the reaction, and slight improvement was observed. Because of the low yields, the UV-Vis absorbance of the reactants was analyzed. Figure 4 shows that 2-furfural and 5-bromo-2-furfural compete for the same UV light. If 2-furfural is derivatized into 2-(2-furyl)-1,3-dioxolane, the UV absorbance spectrum shifts to lower wavelengths and will not compete for the UV light necessary for the reaction. Furan also demonstrates a similar UV absorbance spectrum and does not compete with 5-bromo-2-furfural for UV light.

If 2-(2-furyl)-1,3-dioxolane is irradiated in the presence of 5-bromo-2-furfural with 100 times the anionic exchange resin, 1,3-dioxolane-5-carboxaldehyde-[2,2'-bifuran] (**2F**, Table 3) forms quickly initially and then slows. The reaction slows because HBr formed during the reaction is not removed quickly enough and the 2-(2-furyl)-1,3-dioxolane reverts back to 2-furfural. This occurs when the pH of the solution drops below 4.0. As this furfural is formed, the small amounts of furfural begin to absorb the UV light necessary for the reaction to occur, and the reaction begins to behave like the reaction with only furfural. Furan, on the other hand, does not compete with 5-bromo-2-furfural for UV light. Therefore, high yields of [2,2'-bifuran]-5-carboxaldehyde (**4F**, Table 3) can be achieved in as little as 18 h.

Synthesis of difuran derivatives relies on two factors during reaction. First, the formation of HBr must be minimized by a high quantity of acid-scavenging resin. Second, 5-bromo-2-furfural must not be

Table 3. Synthesis of various difuran derivatives via photolytic coupling.



| Entry | Substrate (R-group) | Rxn Time [h] | Light Source | Yield | Product |
|-------|---------------------|--------------|--------------|-------|---------|
| 1F | | 18 | 254 nm | 50 | |
| 2F | | 72 | 306 nm | 50 | |
| 3F | | 24 | 254 nm | 10 | |
| 4F | | 48 | 306 nm | 5 | |

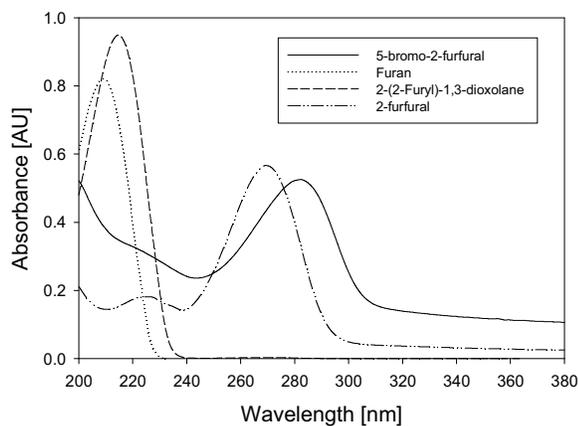


Figure 4. The UV-Vis spectra of 5-bromo-2-furfural (———), furan (.....), 2-(2-furyl)-1,3-dioxolane (- - - -), and 2-furfural (— · · -).

in competition for UV light with reactants. If these two factors are controlled, high yields of bifuran products can be realized.

3.2 Dynamic Mechanical Analysis

Results from DMA indicate that the T_g and modulus of the DA1/HEMA copolymers decrease with an increase in DA1 content. Also, at higher temperatures, it appears the polymer could be losing structural integrity by reverting back to the bismaleimide/furan ring from which it was synthesized and destroying the cross-links in the polymer.

3.3 Shrinkage stress

BA1 exhibited more shrinkage stress than all the DA1 samples. As the amount of HEMA is increased, the shrinkage stress of the material also increased as shown in Figure 5. When compared to DMA data shown above, the shrinkage stress increases with an increase in the glass transition temperature (T_g) and the modulus. These factors indicate that, although more DA1 in a sample decreases shrinkage stress, it is probably only a factor of the modulus of the material.

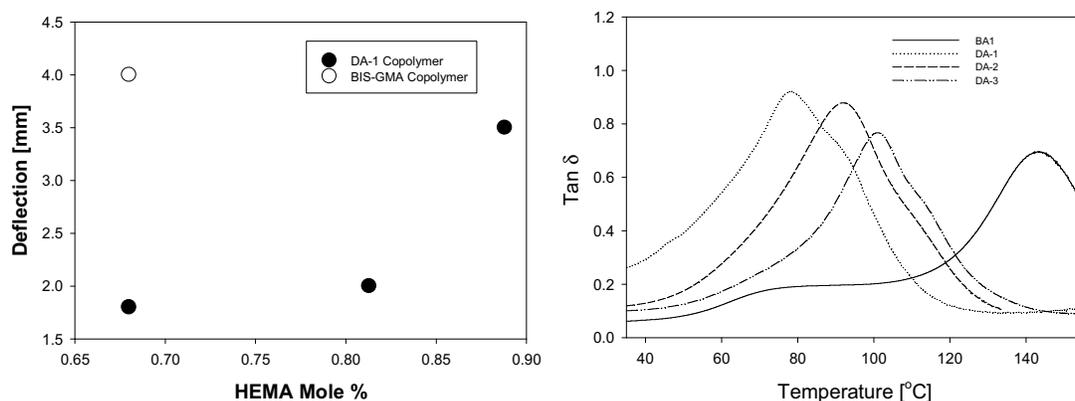


Figure 5. Changes in shrinkage stress with HEMA mol% in DA1 and Bis-GMA formulations (left). Tan δ curves show that T_g steadily decreases with increasing percentage of DA-1 in the sample and that T_g is much lower than that of the Bis-GMA samples (right).

4. Conclusions

Difuran molecules synthesized by the green photochemical coupling method show promise for applications in many fields. If the appropriate initiating light and reactant combination are used, difuran building blocks can be synthesized from a variety of furan, thiophene, and benzyl derivatives. Physical properties of the DA1/HEMA copolymers are promising and could prove useful in a number of applications. Monomers for step-growth and addition polymerization will be synthesized from these compounds, and the physical properties of the resulting polymers will be analyzed using DMA.

5. Acknowledgements

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6. References

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