

# Degradation Behavior of Poly(2,3-Dihydrofuran)

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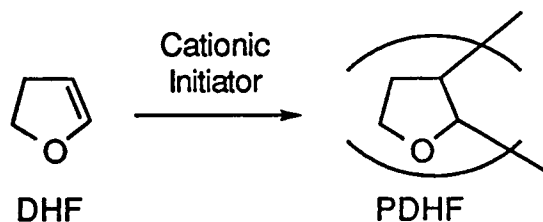
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## SYNOPSIS

Degradation behavior of poly(2,3-dihydrofuran) (PDHF) was investigated. PDHF was prepared by cationic polymerization of 2,3-dihydrofuran (DHF) with boron trifluoride ( $\text{BF}_3$ ) in toluene at  $-78^\circ\text{C}$ . The rate of the degradation depended upon the relative surface area of PDHF samples. The larger the surface area of the PDHF sample, the faster the molecular weight decreased. An oxidative degradation mechanism was confirmed, because lactone and acetal structures were detected in the degraded PDHF samples by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, and ESR spectra. No degradation proceeded under a nitrogen atmosphere. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Poly(2,3-tetrahydrofurandiyl) (PDHF) has been reported to be obtained by polymerization of 2,3-dihydrofuran (DHF) with cationic initiators such as boron trifluoride ( $\text{BF}_3$ ),<sup>1,2</sup> diethyl aluminum chloride,<sup>3</sup> iodine,<sup>4</sup> acetyl perchlorate (Scheme 1).<sup>4</sup>



Scheme 1

PDHF is interesting material that shows high glass transition temperature ( $T_g$ ) and molecular weight.<sup>5</sup> Properties of PDHF have been well studied by Moore et al. They have studied PDHF as a candidate for use as a battery separator in secondary lithium batteries.<sup>6</sup> Their study on computer modeling of the configuration of PDHF revealed that the lowest energy conformations for the erythrodiisotactic and threodisyndiotactic structures are extended chains

and that helical conformers represent energy minima for the erythrodisyndiotactic and threodiisotactic forms.<sup>7,8</sup> They have also examined oxidation of PHF to afford hydroperoxides<sup>9</sup> and ring-opening reaction of PDHF by hydroiodic acid.<sup>10,11</sup> Recently, we have investigated the cationic polymerization behavior of DHF and the relationship between the  $T_g$  and the tacticity of the polymer.<sup>12</sup> From the  $^{13}\text{C}$  NMR spectral and molecular mechanical analyses, it was confirmed that the  $T_g$  of PDHF increased as the content of *cis* isomer increased. In the course of the study on cationic polymerization behavior of DHF, we have found that PDHF is degraded under air. Moore et al. also suggested that PDHF derivatives were degraded by oxygen,<sup>9</sup> however, the detailed degradation behavior and mechanism of degradation are still not clear. Because PDHF contains the tetrahydrofuran structure, which is easily oxidized to peroxide, PDHF may be an oxidatively degradable polymer. In this article, the degradation behavior and mechanism of degradation of PDHF are explored.

## EXPERIMENTAL

### Measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at  $27^\circ\text{C}$  on a JEOL JNM-GX-500 spectrometer with tetramethylsilane (TMS) as an internal standard in deuterio chloroform. FT-IR spectra were obtained

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**Table I** Thermal Stability of PDHF<sup>a</sup>

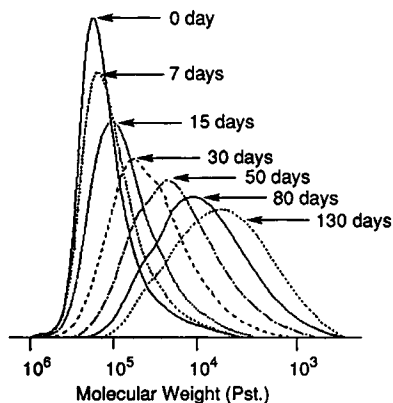
	In Nitrogen	In Air
5% weight loss temperature <sup>b</sup> (°C)	360	345
remaining wt % at 300°C	98	97
remaining wt % at 400°C	76	57

<sup>a</sup> Determined by TGA.<sup>b</sup> Heating rate of 10°C/min.

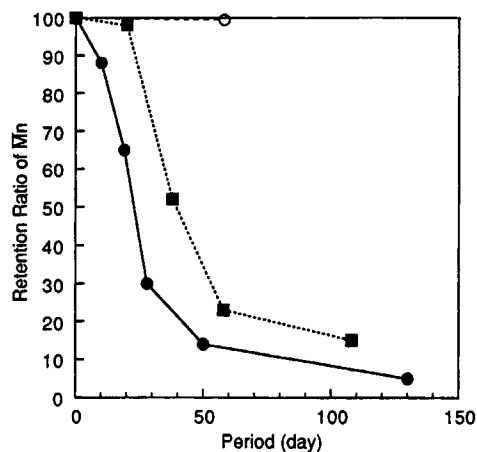
with a Digilab FTS-20C/T at 25°C. ESR spectra were recorded on a JEOL JES-FE2XG. Molecular weight and its distribution ( $\bar{M}_w/\bar{M}_n$ ) were determined by gel permeation chromatography (GPC) on a Shimadzu LC-6A system with a data processor, equipped with three polystyrene gel columns (Shim-pack, HSG-20H, HSG-40H, and HSG-60S), with tetrahydrofuran (THF) as the eluent, flow rate 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Thermogravimetric analyses (TGA) were performed on a Rigaku Denki TG/DTA8075D1. Five percent weight loss temperature by TGA was determined at a heating rate of 10°C/min in nitrogen or air. Specific surface was measured with a Yuasa Ionics Quantasorb QS-13. Percent transmittancy was measured with a Hitachi spectral transmittance photometer HITACHI 330. Bending strength was measured according to JIS K7203 (test piece; plate of 1 mm thickness molded at 240°C by a heat-pressing machine).

## Materials

Initiator BF<sub>3</sub> (Hashimoto Chemical Industries) was used as received. BF<sub>3</sub> solutions were prepared by



**Figure 1** Change of GPC curves of PDHF in air at room temperature. Sample; specific surface area 9.2 m<sup>2</sup>/g,  $\bar{M}_n$  before degradation of 85,000. Polymer was obtained in the polymerization with BF<sub>3</sub> at -78°C.

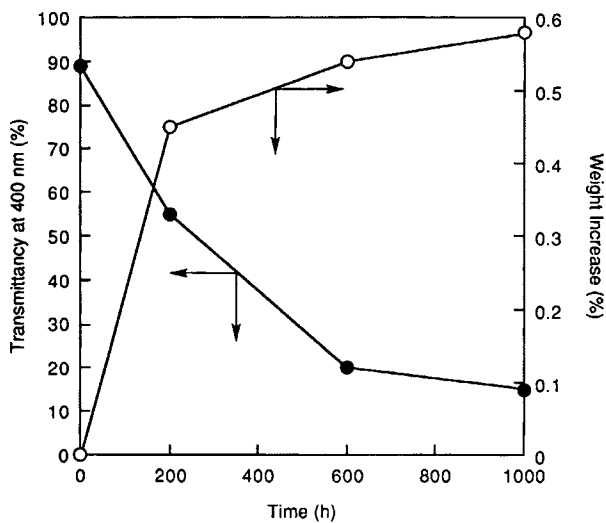


**Figure 2** Time-molecular weight curves of PDHF with several forms at room temperature. ○; plate in 1 mm thickness molded by a heat pressing machine (calculated specific surface area 0.0018 m<sup>2</sup>/g). ■; Sample obtained by crashing the heat pressed plate (specific surface area 0.09 m<sup>2</sup>/g). ●; Reprecipitated polymer (without molding, specific surface area 9.2 m<sup>2</sup>/g,  $\bar{M}_n$  85,000. The polymer used was obtained in the polymerization with BF<sub>3</sub> at -78°C.

bubbling BF<sub>3</sub> into solvents. The concentration of a BF<sub>3</sub> solution was determined by titration of the mixture of the BF<sub>3</sub> solution and water (volume ratio, 1 : 5) using standard hydrochloric acid with phenolphthalein as an indicator.

## Polymerizations of DHF

General Procedure: to a 14.5 mM solution of BF<sub>3</sub> in toluene (10 mL), DHF (2.0 g, 29 mmol) was added



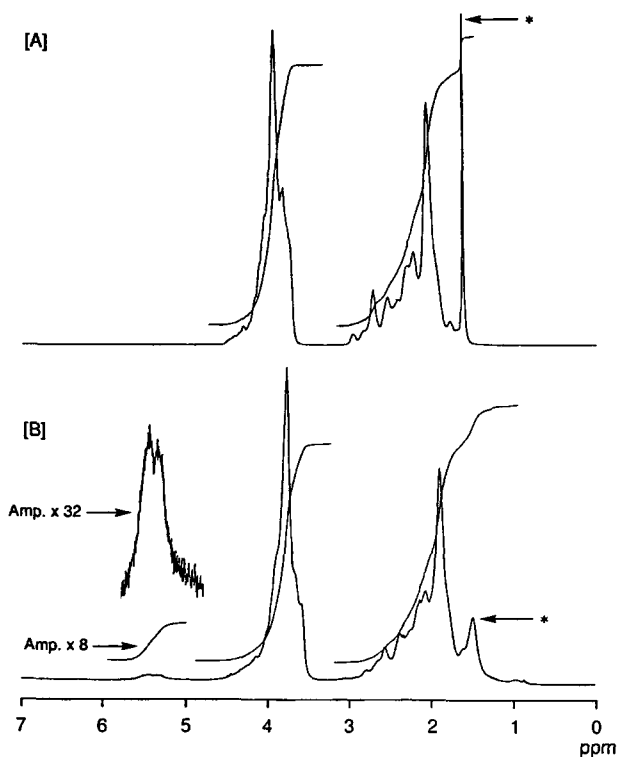
**Figure 3** Time-transmittancy and time-weight increase curves of PDHF plate (1 mm thickness molded at 240°C by a heat-pressing machine) in air at 100°C.

dropwise at  $-78^{\circ}\text{C}$ . After that, the reaction mixture was stirred for 48 h. Polymerization was stopped by the addition of 1 M ammonia solution in methanol (0.5 mL, 0.5 mmol). The resulting mixture was diluted with toluene (10 mL) and precipitated into methanol (400 mL) to isolate a solvent-insoluble polymer. Conversion 30%, yield 0.50 g (25%),  $\bar{M}_n$ ; 44600,  $\bar{M}_w/\bar{M}_n$ ; 2.03,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.4–2.9 (broad s, 3 H), 3.5–4.5 (broad s, 3 H) ppm,  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25–32, 39–50, 65–69, 77–86 ppm, IR (cast film from THF) 2950, 2860, 1455, 1200, 1062, 920, 690  $\text{cm}^{-1}$ .

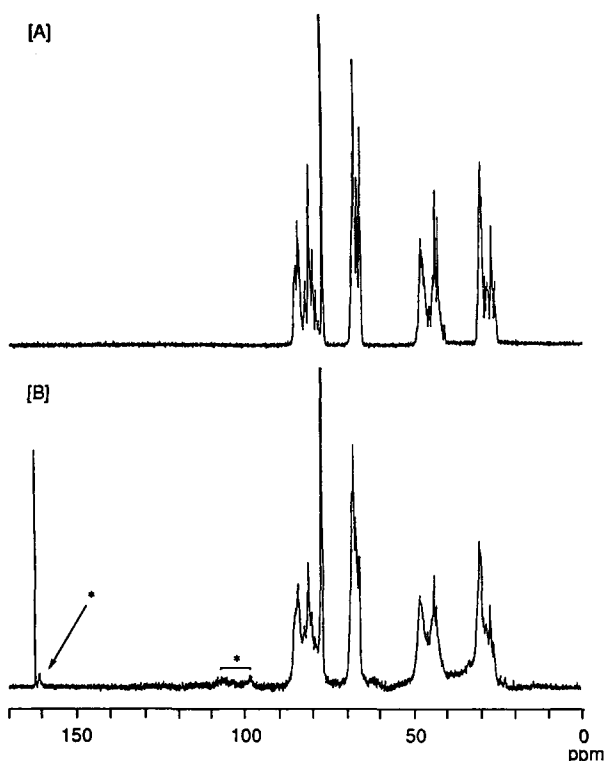
ANAL. Calcd for  $\text{C}_4\text{H}_6\text{O}$ : C, 68.55; H, 8.63. Found: C, 68.75; H, 8.88.

### Degradation of PDHF

Degradation of PDHF at room temperature was carried out in an open flask under air. Degradation of PDHF plate (1 mm thickness molded at  $240^{\circ}\text{C}$  by a heat pressing machine) at  $100^{\circ}\text{C}$  was carried out in an air oven.



**Figure 4**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 500 MHz) of PDHF before and after degradation. Polymer was obtained in the polymerization with  $\text{BF}_3$  at  $-78^{\circ}\text{C}$ . (A) Before degradation,  $\bar{M}_n$  38,000. (B) After degradation,  $\bar{M}_n$  7600. \*: Signal derived from water.



**Figure 5**  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ , 125 MHz) of PDHF before and after degradation. (A) Before degradation,  $\bar{M}_n$  38,000. (B) After degradation,  $\bar{M}_n$  7600. \*: Signal derived from degraded structure.

## RESULTS AND DISCUSSIONS

### Degradation of PDHF

First, TGA under air and nitrogen was carried out to obtain basic information on the thermal stability of PDHF. The results are summarized in Table I. PDHF was more unstable in air than in nitrogen. Therefore, some oxidative degradation of PDHF should proceed in air. To make this point clear, change of molecular weight of PDHF under air was investigated. The form of PDHF obtained by the polymerization with  $\text{BF}_3$  at  $-78^{\circ}\text{C}$  followed by reprecipitation into methanol was fibrous. The specific surface area of the polymer reprecipitated was as large as  $9.2 \text{ m}^2/\text{g}$ . The number average molecular weight ( $\bar{M}_n$ ) of the polymer decreased from 85,000 to 4,300 after 130 days in air at room temperature (Fig. 1). No such decrease of the molecular weight was observed in nitrogen. Time–molecular weight curves of a PDHF molded plate in 1 mm thickness and a sample obtained by crushing the plate are shown in Figure 2 with that of the polymer just after isolation by reprecipitation. The degradation behavior of the polymers was related with their specific

surface area. The rate of degradation of the 1 mm plate was very slow compared to the others. Because the fibrous polymer obtained by reprecipitation from this plate showed the same rate of degradation as the polymer before heat molding, the thermal history of the polymer should not be related to the rate of degradation.

Change in percent transmittancy at 400 nm and weight increase of the PDHF plate in air at 100°C are shown in Figure 3. The colorless transparent PDHF plate became gradually brownish with decrease of transmittancy at 400 nm. Under the same condition, bisphenol-A polycarbonate (Teijin Chemical, Panlite AD5503) showed no decrease of transmittancy. A weight increase of the plate should be caused by the absorption of oxygen. Bending strength of the plate decreased from 1,250 to 700 kg/cm<sup>2</sup> after 1,000 h exposure in air at 100°C.

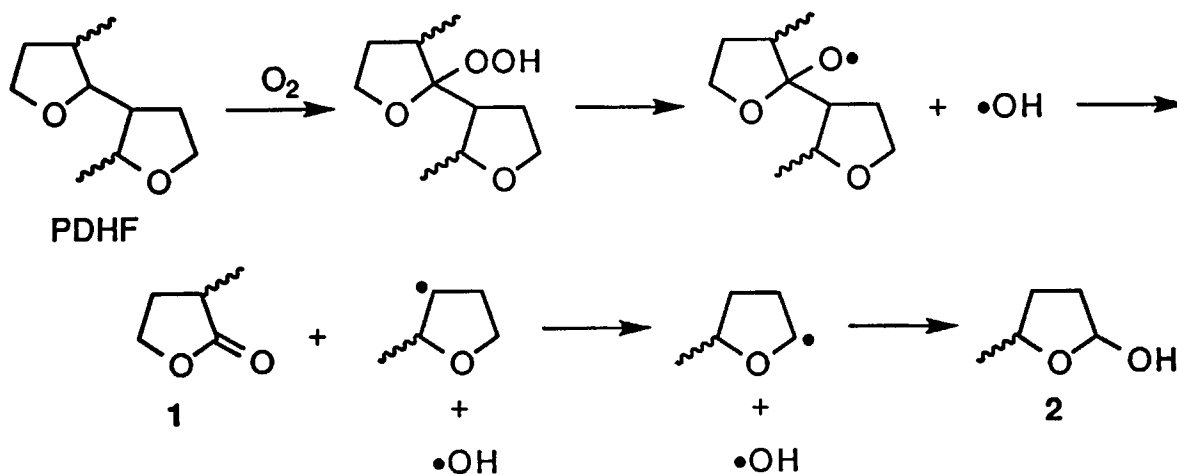
### Degradation Mechanism

<sup>1</sup>H and <sup>13</sup>C NMR spectra of PDHF before and after degradation were measured to investigate the degradation mechanism. A signal at 5.5 ppm, which was not observed in the <sup>1</sup>H NMR spectrum before degradation, was observed when the polymer molecular weight decreased to 20% of the original (Fig. 4). Signals at 97 ~ 106 and 160 ~ 162 ppm assigned to acetal and lactone carbonyl carbons, respectively, were observed in the <sup>13</sup>C NMR spectrum of the degraded polymer [Fig. 5(B)]. A strong carbonyl ab-

sorption was observed at 1740 cm<sup>-1</sup> in the IR spectrum of the degraded polymer.

Because the rate of degradation depended on the surface area (Fig. 2), and an increase of weight was observed in air (Fig. 3), and acetal and lactone units were contained in the degraded polymer (Figs. 4 and 5), the degradation of the polymer should proceed radically by main chain fission resulting from oxygen attack. A radical signal was observed in the ESR spectra in the polymer and the intensity of the signal increased as the measuring temperature was raised (Fig. 6). The assignment and determination of the signal could not be carried out because of its broadness. The heat-molded sample showed larger intensity than the sample before molding.

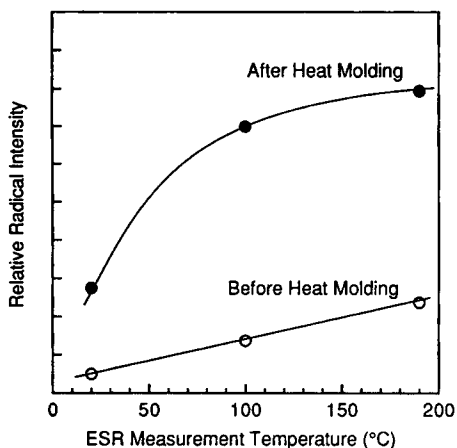
Moreover, an exothermic peak at 160°C and 1.2% weight increase was observed in the temperature-raising process in TGA of PDHF in air. No such peak in TGA or weight increase was observed at all in nitrogen. The presence of peroxide species in the polymer was confirmed by a titration with potassium iodide and sodium thiosulfate. The content of peroxides in the polymer calculated from the titration was 0.05% just after isolation by reprecipitation. The peroxide content in the polymer whose  $\bar{M}_n$  has decreased to 26% was 0.8%. From these results, a plausible degradation mechanism of PDHF is shown in Scheme 2. At first, peroxide forms by addition of oxygen to the  $\alpha$ -position of the ether oxygen, and then decomposition and rearrangement of the peroxide proceed to afford lactone (1) and acetal units (2).



Scheme 2

From the integration ratio of the <sup>1</sup>H NMR spectrum [Fig. 4(B)], both the contents of 1 and

2 were calculated to be 4% based on the repeating unit in the polymer whose molecular weight de-



**Figure 6** Relative intensity of radical signal in ESR spectra of PDHF at various temperature.

creased to 20%. A crosslinking reaction was also confirmed at high temperature, with the content of THF-soluble polymer exposed to air at 100°C for 15 h being only 23% and its  $\bar{M}_n$  only 15% of the original. The IR spectrum of the THF-insoluble part showed carbonyl absorption at 1740  $\text{cm}^{-1}$  to indicate the formation of lactone group. The content of THF-soluble part of the polymer exposed to the same condition for 56 h decreased to 12%.

## CONCLUSION

Degradation behavior of poly (2,3-dihydrofuran) (PDHF) obtained in cationic polymerization of 2,3-dihydrofuran (DHF) and the mechanism of degradation were studied. The molecular weight of PDHF decreased under air, and the larger the surface area of the PDHF sample was, the larger the rate of decrease of molecular weight. Decrease in transmittancy and bend strength and increase of weight were observed corresponding to the de-

crease of the molecular weight. From the analyses of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, and ESR spectra, an oxidative degradation mechanism was confirmed. Attempts to control the rate of degradation, and investigations of thermal, mechanical, and optical properties, and so on, will be disclosed elsewhere.

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