

# Synthesis and Cyclization of Aromatic Polyhydroxyamides.

## 1. Model Compound Study

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### 1. INTRODUCTION

Aromatic polybenzoxazoles have been known since 1964 as a class of aromatic heterocyclic polymers that exhibit excellent thermal stability<sup>1-3</sup>. Polyhydroxyamides (PHA), precursor polymers to PBO, can cyclize to form stable heterocyclic polymers with the simultaneous release of small molecules, which can be expected to act as a fire quencher.

In the present study, we examined the possibility of cyclization of fluorinated functional group during heating. We synthesized the model compounds of the PHA and the trifluoromethyl group containing PHA and investigated the cyclization chemistry of them.

### 2. EXPERIMENTAL

#### 2.1 Materials

o-Aminophenol, benzoyl chloride, o-trifluoromethoxyl aniline, trifluoroacetic anhydride were obtained from Aldrich Chemical Company. N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), Tetrahydrofuran(THF) were purified by distillation methods under reduced pressure. Pyridine(Py), Triethylamine(TEA), 4-pyrrolidinopyridine(PLP), 4-dimethylaminopyridine(DAP) were selected for catalysts.

#### 2.2 Syntheses of the model compounds

**Synthesis of N-(2-hydroxyphenyl) benzamide** : N-(2-hydroxyphenyl)amide(HPB) was obtained by reacting 2-aminophenol with benzoyl chloride in DMAc. The solution was stirred at 0°C for one hour, then at room temperature for 5 hours. The precipitation was obtained by crystallization into water dried in vacuum.

**Synthesis of N-(2-trifluoromethoxyphenyl) benzamide** : N-(2-trifluoromethoxy-

phenyl) benzamide (FMB) was obtained by reacting o-trifluoromethoxyaniline with benzoyl chloride in DMAc. The solution was stirred at 0°C for one hour, then at room temperature for 5 hours. The precipitation was obtained by crystallization into water dried in vacuum.

**Synthesis of 2-benzamidophenyl trifluoroacetate :** 2-benzamidophenyl trifluoroacetate (BPF) was obtained by derivatizing HPB with trifluoroacetic anhydride and 4-pyrrolidinopyridine as a acid acceptor at room temperature in DMF. After 3 hours the mixture was poured into water dried in vacuum.

### 2.3 Cyclization of the model compounds

The model compounds was heated in a sealed test tube under vacuum at temperatures from 250°C to 300°C for 1 and 5 min.

### 2.4 Characterization of the model compounds

The structural analyses of model compounds were performed by <sup>1</sup>H and <sup>19</sup>F-NMR spectroscopy using a BRUKER DPX 300 NMR Spectrometer on a DMSO-*d*<sub>6</sub> solution. The thermal analyses were performed by DSC 2910(TA Instruments) under N<sub>2</sub> atmosphere with a heating rate of 20°C/min.

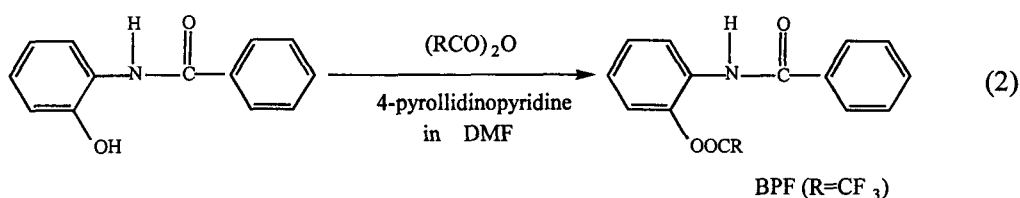
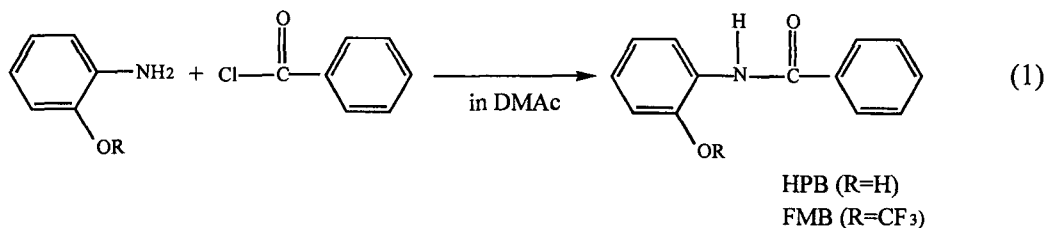
## 3. RESULTS AND DISCUSSION

### 3.1 Syntheses of model compounds

Scheme (1) represents the generalized equation for the syntheses of HPB and FMB. The acylation of hydroxyl group in HPB have been tested by various solvent and catalyst combinations. Table 1 shows the results. The degree of substitution was calculated by the ratio of amide and hydroxyl group peak area from <sup>1</sup>H-NMR spectra. As shown in Table 1, we found that the reactivity of hydroxyl group with trifluoroacetic anhydride might be the best when PLP and DMF was used. Scheme (2) is the generalized equation for this reaction. Three kinds of the <sup>1</sup>H-NMR spectra of the model compounds are shown in Fig. 1, which indicates that model compounds have been successfully synthesized. For FMB and BPF, the peaks of the protons of the N-phenyl group have been shifted downfield because of the substitution of the hydroxyl group.

### 3.2 Cyclization of model compounds

The cyclizations of model compounds HPB, FMB, and BPF were examined by NMR Spectroscopy. Because the model compounds were volatile after melting, the cyclization reactions were performed in a sealed test tube under vacuum.



As shown in Fig. 2, the cyclization of HPB was completed at 370°C for 5min. Fig. 3 shows the <sup>1</sup>H-NMR spectra of BPF and FMB heated at 370°C for 5 min. In case of BPF, amide proton peak and fluorine peak of trifluoromethyl ester group were not found. On the other hand, the amide proton peak and fluorine peak of trifluoromethyl ether group remained for FMB. This means that trifluoromethyl ester type derivative can cyclize, while the trimethyl ether one cannot.

#### 4. CONCLUSION

The hydroxyl group of HPB could be substituted with trifluoroacetic anhydride with the aid of the catalyst such as PLP in DMF. Trifluoromethyl ether and ester group containing model compounds were synthesized.

BPF and HPB can cyclize at 370°C for 5min. However, the FMB, in which the trimethyl ether group is thought to be too strong to be ruptured, can't cyclize.

#### REFERENCES

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Table 1. The degree of substitution of hydroxyl group

Catalyst	Solvent		
	DMAc	DMF	THF
Py <sup>a</sup>	0	43	0
PLP <sup>b</sup>	0	100	0
TEA <sup>c</sup>	33	90	0
TEA/DAP <sup>d</sup>	75	80	78

<sup>a</sup>Pyridine.

<sup>b</sup>4-Pyrrolidinopyridine.

<sup>c</sup>Triethylamine.

<sup>d</sup>4-Dimethylaminopyridine.

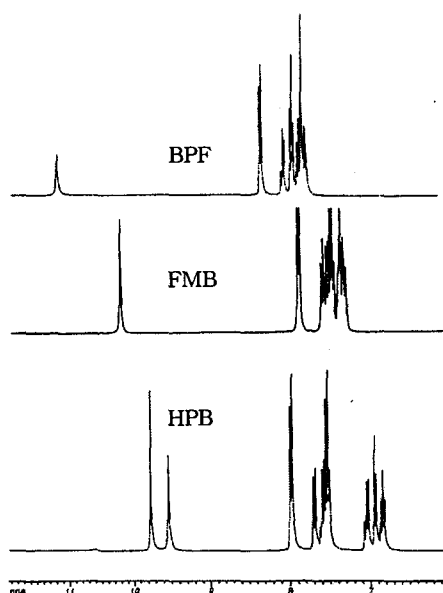


Figure 1. <sup>1</sup>H-NMR spectra of model compounds.

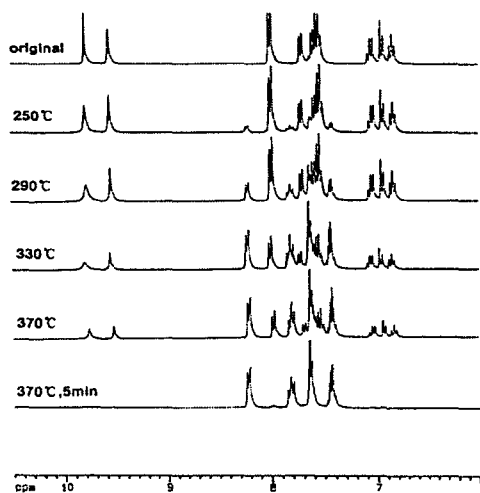


Fig. 2. <sup>1</sup>H-NMR spectra of HPB heated at various temperatures.

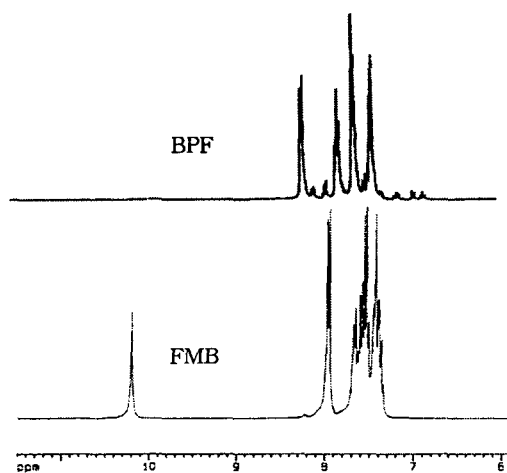


Fig. 3. <sup>1</sup>H-NMR spectra of BPF and FMB heated at 370 °C for 5 min.