

# Synthesis and Cyclization of Aromatic Polyhydroxyamides.

## 2. Polyhydroxyamides Containing Trifluoromethyl Group

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### 1. INTRODUCTION

Wholly aromatic polybenzoxazoles (PBO) are well established as high performance materials with excellent thermal stability and mechanical properties<sup>1</sup>. Heterocyclic precursor polymers such as polyhydroxyamides (PHA) have been interested in the field of high performance flame retardant polymers. The PHAs can be converted to PBOs when ignited.

At the same time, they release water molecules as products of the cyclization reactions which act as a fire quencher. The molecules released during cyclization are very important in these flame retardant polymers. If the hydroxyl groups of PHA are derivatized with halogenated compounds, they may act as more effective extinguishers under flame conditions.

In this paper, we have synthesized the PHA and the PHA derivatives containing trifluoromethyl ester group and checked the cyclization chemistry of them.

Derivatization was performed under the reaction conditions obtained from the model compounds study.

### 2. EXPERIMENTAL

#### 2.1 Materials

N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), Isophthaloyl chloride (IPC), trifluoroacetic anhydride, and 4-pyrrolidinopyridinewere obtained from Aldrich Chemical Company. 3,3'-Dihydroxybenzidine (DHB) was obtained TCI America, and the chemicals were purified before use.

#### 2.2 Synthesis of polyhydroxyamide<sup>2,3</sup>

DHB was dissolved in anhydrous DMAc. The solution was cooled to 0°C, and IPC dissolved in DMAc are added dropwise with stirring. The solution was stirred for 1 hour at 0°C, and additional 5 hours at room temperature. The reaction mixture was poured into ethanol with stirring. The polymer was filtered and dried in vacuum at 70°C for 24 hours.

#### 2.3 Derivatization of polyhydroxyamide

PHA was derivatized with trifluoroacetic anhydride. PHA and 4-pyrrolidinopyridine were dissolved in DMF with the aid of lithium chloride and trifluoroacetic anhydride was added dropwise at room temperature. After 3 hour, the reaction mixture was poured into water with stirring, and derivatized polymers were filtered and dried in vacuum at 70°C for 24 hours.

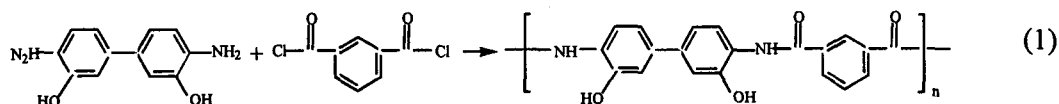
## 2.4 Characterization of PHA and derivatized PHA

The structural analyses of PHA and derivatized PHA were performed by  $^1\text{H}$  and  $^{19}\text{F}$ -NMR spectroscopy using a BRUKER DPX 300 NMR Spectrometer on a DMSO- $d_6$  solution. The thermal analyses performed by du Pont DSC 2910 and Perkin Elmer TGA-7 under  $\text{N}_2$  atmosphere with a heating rate of 20°C/min.

## 3. RESULTS AND DISCUSSION

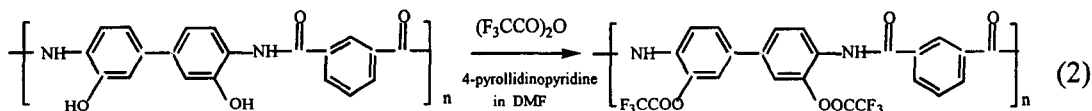
### 3.1 Synthesis of PHA

The reaction of DHB and IPC is a simple condensation reaction. Scheme (1) represents the generalized equation for the syntheses of PHA.



### 3.2 Synthesis of derivatized PHA

The ester derivatives can cyclize on heating as confirmed by the model compound study. Hence, we have tried to introduce the trifluoromethyl ester pendant group on hydroxyl group. PHA was partly derivatized with trifluoromethyl acetyl group according to the method mentioned in the experimental method. Scheme (2) represents the generalized equation for the syntheses of derivatized PHA.



### 3.3 Characterization

Fig. 1 shows DSC thermograms of PHA(P-0) and 48(P-0.48), 91%(P-0.91) derivatized PHA. We could find that P-0 had the peak at 370°C due to the cyclization caused by -OH group, and P-0.48 had peaks at 250°C and 320°C due to the cyclization trifluoromethyl ester group and -OH group, respectively. In P-0.91, the area of the low temperature peak due to the cyclization of trifluoromethyl ester group increased, while that of the high temperature peak due to -OH group decreased.

Fig. 2 shows  $^1\text{H}$ -NMR spectra of PHA(P-0) and 91% derivatized PHA(P-0.91). In these

spectra, P-0 has two singlets at 10.2 and 10.7 ppm due to -OH and -NH group, whereas in P-0.91, there shows a singlet at 11.4 ppm due to trifluoromethyl ester group.

Fig. 3 shows the TGA thermograms of PHA and trifluoromethyl ester derivatives. Each TGA thermogram shows the typical two-step weight loss during heating. The first weight loss at 150~400°C region is due to cyclization, and the second one at 550~700°C is due to the thermal degradation of the cyclized polymer. As can be seen in Fig. 1, the weight loss due to cyclization increase with degree of derivatization because of the higher molecular weight of trifluoroacetic acid than water.

The char yield is sometimes used as an indication of flammability of a polymer. Since the PHA and its derivatizes release molecules during cyclization, the char yield can be seriously affected by the weight loss due to cyclization. Hence, we compared the char yield which was calculated after cyclization. Table 1 shows the char yield data obtained by both direct observation at 900°C and calculation between 500 and 900°C. The samples P-0.58 and P-0.91 have nearly the same level of char yield as the sample P-0, which implies that the PBOs formed after cyclization have similar thermal stability.

Table 1. Observed and calculated char yields of its derivative

Samples	Substitution(%)	Observed(%)	Calculated(%)
P-0	0	55	65
P-0.58	58	38	67
P-0.91	91	32	66

### 3.4 Cyclization of PHA

Cyclization behaviors of PHA were examined by using DSC. Fig. 5 shows DSC curves of PHA cyclized at various temperature. The peak area at 370°C was decreased with increasing temperature, which indicated that the endothermic peak was due to cyclization reaction.

The effect of time and temperature on degree of cyclization was measured by means of DSC. Fig. 6 shows the results. As shown Fig. 6, the maximum cyclization varied with the temperature, for example, 95% at 350°C, 80% at 330°C.

## 4. CONCLUSION

Polyhydroxyamide was readily synthesized, and derivatized with trifluoromethyl acetate, it can't be completely derivatized by using pyrrolidinopyridine as catalyst.

The trifluoromethyl ester group containing PHA shows similar char yields calculated from the residual weight ratio between 500 and 900°C as for the underivatized PHA, which means that the derivatized PHA has similar thermal stability as the underivatized PHA after cyclization.

PHA represents 95% degree of cyclization at 350°C, while 80% at 330°C.

## REFERENCES

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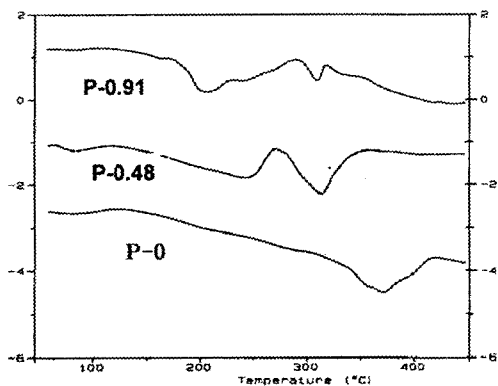


Fig. 1. DSC thermograms of derivatized PHA.

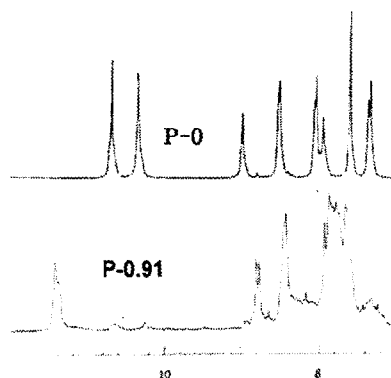


Fig. 2.  $^1\text{H-NMR}$  spectra of derivatized PHA.

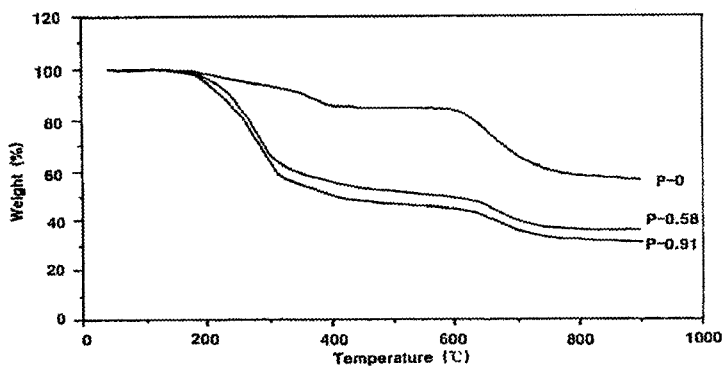


Fig. 3. TGA thermograms of trifluoromethyl derivatized PHA.

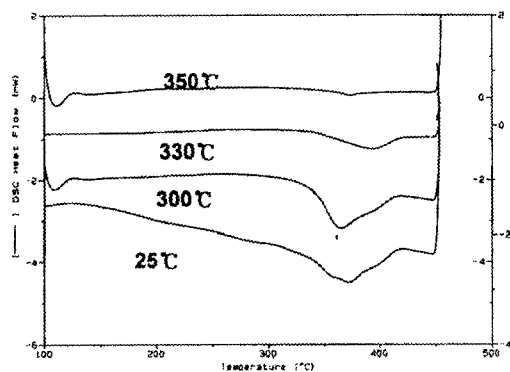


Fig. 4. DSC curves of PHA cyclized with various temp. for 60min.

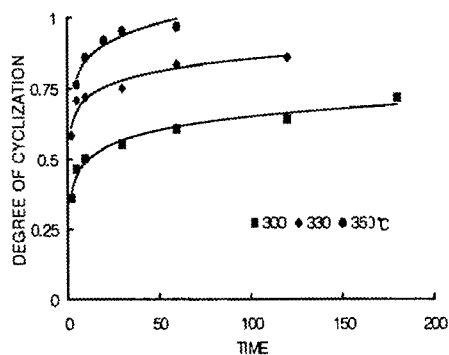


Fig. 5. Degree of cyclization on temperature and time.