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Synthesis and Cyclization of Aromatic Polyhydroxyamides Containing Trifluoromethyl Groups

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Abstract: Polyhydroxyamides derivatized with trifluoromethyl ether and trifluoromethyl ester groups were investigated as possible candidates for a new flame retardant polymer. Model compounds for these derivatized polyhydroxyamides were synthesized and their cyclization chemistry was investigated. The model compound study revealed that trifluoromethyl ester group containing model compounds can cyclize on heating, while trifluromethyl ether group containing model compounds cannot. The non-fluorinated ester and ether derivatives behaved similarly. The trifluoromethyl ester derivatized polyhydroxyamides were synthesized according to the procedures for the model compounds. TGA characterization revealed that the fluorinated polymers have nearly same thermal stability as the underivatized PHA after cyclization.

Keywords: Polyhydroxyamides, Precursor, Polybenzoxazoles, Model compounds, Thermal cyclization, Derivatization, Trifluoromethyl group

Introduction

Flame retardancy of polymeric materials is one of the very important properties of high performance polymers, especially in the field of aircraft application. Recently, our group has reported a new way to obtain high performance flame retardant polymers using precursors to heterocyclic polymers, which, under fire conditions, cyclize to form stable heterocyclic polymers with the simultaneous release of small flame extinguishing compounds[1]. Aromatic polyhydroxyamides are examples of these categories. They have good mechanical properties and can be converted to polybenzoxazoles 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. We have tested phosphorous derivatives of polyhydroxyamides, where the released phosphorous compounds were expected to act as better retardant than water. However, the results were not as good as for the underivatized polyhydroxyamides. These results imply that we still need other pendant groups which can be eliminated easily and act as efficient extinguishers under flame conditions.

In the present study, polyhydroxyamides derivatized with trifluoromethyl ether and trifluoromethyl ester groups were investigated as possible candidates for a new flame retardant polymer. Trifluoromethyl ether and ester groups were chosen because they are small halogen-containing groups which would be expected to cyclize. Model compounds for these derivatized polyhydroxyamides were synthesized and characterized in order to select the best polymer derivatization method and investigate the cyclization chemistry of both the trifluoromethyl ether and ester groups. The possibility of cyclization of non-fluorinated methyl ether or ester group containing model compounds was also investigated. Trifluromethyl group containing polyhydroxyamides were synthesized according to the results of the model compounds. TGA characterization of the fluorinated polymers has been obtained.

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Experimental

Source of Raw Materials

N,N-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidinone (NMP), and benzoyl chloride were obtained from Aldrich Chemical Company, and purified by distillation under reduced pressure. 3,3'-Dihydroxybenzidine was obtained from TCI America, and purified by recrystallization from ethanol/water/DMAc mixture. Isophthaloyl chloride, *o*-aminophenol, *o*-trifluoromethoxyaniline, *o*-anisidine, trifluoroacetic anhydride, acetic anhydride, and 4-pyrrolidinopyridine were obtained from Aldrich Chemical Company.

Characterization Techniques

^{1}H-NMR analysis was conducted on a BRUKER DPX 300 Nuclear Magnetic Resonance Spectrometer. Deuterated dimethylsulfoxide (DMSO-d_6) was used as an NMR solvent. The melting temperatures were measured by Perkin Elmer DSC-7 under nitrogen purging with a heating rate of 20 °C/min. Perkin Elmer TGA-7 was used to determine the thermal stability and thermal cyclization behavior of samples. TGA experiments were conducted under nitrogen with a heating rate 20 °C/min. Intrinsic viscosities of the polymer were measured in NMP using an Ubbelohde viscometer at room

temperature. Since the model compounds can vaporize after melting, cyclization experiments were conducted in sealed ampules. Samples were heated in a salt bath to a desired temperature and then cooled to room temperature.

Model Compound Syntheses

Synthesis of N-(2-hydroxyphenyl)benzamide

N-(2-hydroxyphenyl)benzamide (HPB) was synthesized by reacting 2-aminophenol with benzoyl chloride in DMAc. 2-Aminophenol (10.9 g, 0.1 mol) was dissolved in 100 m*l* of DMAc. The solution was cooled to 0 °C, and benzoyl chloride (14.1 g, 0.1 mol) was added with stirring. The solution was stirred at 0 °C for an hour, then at room temperature for 5 hours. The reaction mixture was poured into water. The precipitate was filtered and dried under vacuum. The product was purified by recrystallization from ethanol/chloroform mixture; yield 19.5 g, 91 %, m.p. 170 °C.

Synthesis of N-(2-trifluoromethoxyphenyl)benzamide

N-(2-trifluoromethoxyphenyl)benzamide (FMB) was synthesized by reacting *o*-trifluoromethoxyaniline with benzoyl chloride in DMAc. *o*-Trifluoromethoxyaniline (1.77 g, 0.01 mol) was dissolved in 30 m*l* of DMAc. The solution was cooled to 0 °C, and benzoyl chloride (1.41 g, 0.01 mol) was added with stirring. The solution was stirred at 0 °C for an hour, then at room temperature for 5 hours. The reaction mixture was poured into water. The precipitate was filtered and dried under vacuum. The product was purified by recrystallization from ethanol/chloroform mixture; yield 2.42 g, 86 %, m.p. 145 °C.

Synthesis of 2-benzamidophenyl Trifluoroacetate

2-Benzamidophenyl trifluoroacetate (BPF) was synthesized by derivatizing HPB with trifluoroacetic anhydride. HPB (0.533 g, 0.0025 mol) and 4-pyrrolidinopyridine (0.555 g, 0.0038 mol) were dissolved in 11 m*l* of *N,N*-dimethylformamide (DMF) at room temperature. Trifluoroacetic anhydride (0.630 g, 0.003 mol) dissolved in 1 m*l* of DMF was added to this solution with stirring. After 3 hours the reaction mixture was poured into water. The precipitate was filtered and dried in vacuum. The product was recrystallized from ethanol/chloroform mixture; yield 0.7 g, 90 %, m.p. 86 °C.

Synthesis of N-(2-methoxyphenyl)benzamide

N-(2-methoxyphenyl)benzamide (MPB) was synthesized by reacting *o*-anisidine with benzoyl chloride in DMAc. *o*-Anisidine (6.158 g, 0.05 mol) was dissolved in 30 m*l* of DMAc, and the solution was cooled to 0 °C. Benzoyl chloride (7.0285 g, 0.05 mol) was added to this solution with stirring. The solution was stirred at 0 °C for one hour, then at room temperature for 5 hours. Unreacted *o*-anisidine and benzoyl chloride were distilled off with DMAc. The product was liquid at room temperature; yield 10.1 g, 89 %, m.p. 68.6 °C.

Synthesis of 2-benzamidophenyl Acetate

2-Benzamidophenyl acetate (BPA) was synthesized by reacting acetic anhydride with *N*-(2-hydroxyphenyl)benzamide in DMF with the aid of 4-pyrrolidinopyridine at room temperature. HPB (0.553 g, 0.0025 mol) and 4-pyrrolidinopyridine (0.555 g, 0.004 mol) were dissolved in 11 m*l* of DMF at room temperature. Acetic anhydride (0.306 g, 0.003 mol) dissolved in 1 m*l* of DMF was added to this solution with stirring. After 3 hours the reaction mixture was poured into water. The precipitate was filtered and dried in vacuum. The product was recrystallized from ethanol/chloroform mixture; yield 0.55 g, 86 %, m.p. 122 °C.

Polymer Syntheses

Synthesis of Polyhydroxyamide

Polyhydroxyamide (PHA) was prepared from the low temperature condensation reaction of 3,3'-dihydroxybenzidine and isophthaloyl chloride in DMAc[2,3]. 3,3'-Dihydroxybenzidine (2.16 g, 0.01 mol) was dissolved in 30 m*l* of anhydrous DMAc. The solution was cooled to 0 °C, and isophthaloyl chloride (2.03 g, 0.01 mol) was added with stirring. The solution was stirred for 1 hour at 0 °C, then at room temperature for 5 hours. The reaction mixture was poured into a large amount of ethanol with stirring. The polymer was filtered and dried in vacuum at 70 °C for 24 hours.

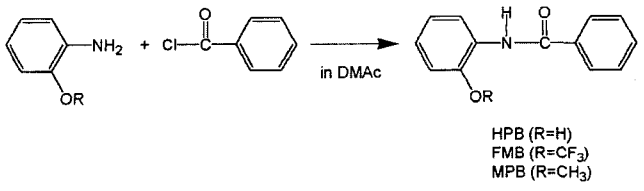
Derivatization of Polyhydroxyamide

Polyhydroxyamide was derivatized with trifluoroacetic anhydride. Polyhydroxyamide (0.693 g, 0.002 mol) and 4-pyrrolidinopyridine (0.685 g, 0.0048 mol) were dissolved in 11 m*l* of DMF with the aid of lithium chloride (0.0357 g, 5 wt% of PHA), and trifluoroacetic anhydride (1.01 g, 0.0048 mol) or acetic anhydride (0.49 g, 0.0048 mol) was added dropwise at room temperature. After 3 hours, the reaction mixture was poured into water with stirring. The derivatized polymers were filtered and dried in vacuum at 70 °C for 24 hours.

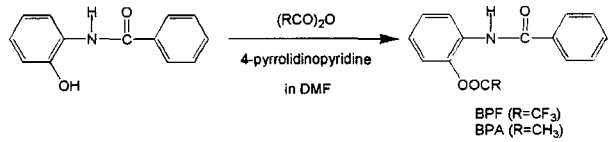
Results and Discussion

Synthesis and Characterization of Model Compounds

The reaction between a primary amine and benzoyl chloride is a simple condensation reaction. Since this reaction was exothermic, an ice bath was used initially for the reaction.



Scheme 1. Synthesis of HPB, FMB, and MPB.



Scheme 2. Synthesis of BPF and BPA.

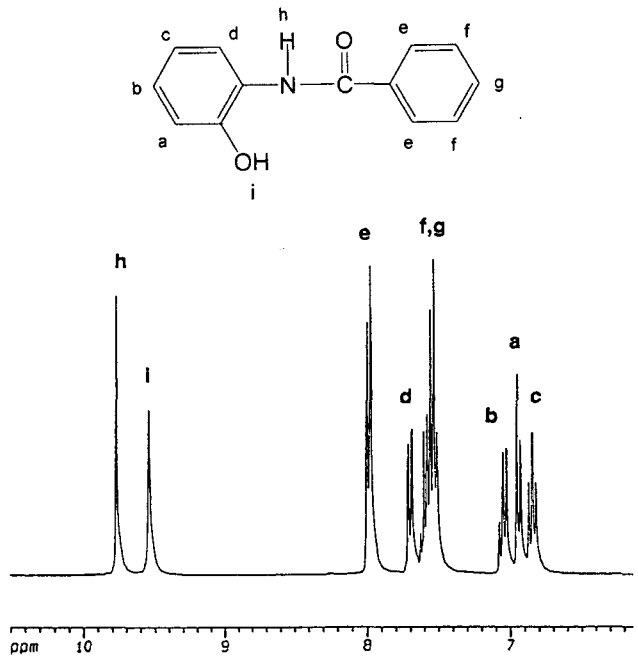
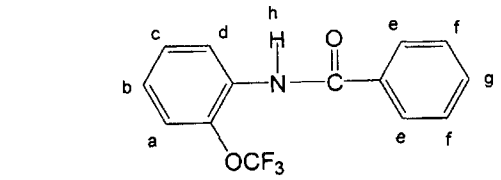


Figure 1. ^{1}H-NMR spectrum of *N*-(2-hydroxyphenyl)benzamide (HPB).

Scheme 1 represents the generalized equation for the syntheses of HPB, FMB, and MPB.

On the other hand, the acylation of hydroxyl group in HPB was more difficult. We have tested various solvents, various acylating agent such as the anhydride or acyl chloride, and various acylation catalysts[4-10]. From these experiments we found that reacting HPB with trifluoroacetic anhydride in DMF with 4-pyrrolidinopyridine as an acylating catalyst resulted in a complete reaction within 3 hours at room temperatures. Hence, these reaction conditions were used for all the ester type derivatization reactions of the hydroxyl group. Scheme 2 is the generalized equation for this reaction.

Figures 1 to 3 are the ^{1}H-NMR spectra of HPB, FMB, and BPF, respectively. In Figure 1 there are two singlets (1H each) at 9.75 and 9.5 ppm which are due to amide and hydroxyl protons, respectively, as confirmed by the previous study[1]. The doublet (1H) at 7.95 ppm is the signal of proton **e**. The doublet (1H) at 7.7 ppm is due to proton **d**, and the multiplet (3H) at 7.4-7.6 ppm is due to protons **f** and **g**. The triplets (1H each) at 7.0 and 6.8 ppm are due to protons **b** and **c**, respectively, and the doublet (1H) at 6.95 ppm is



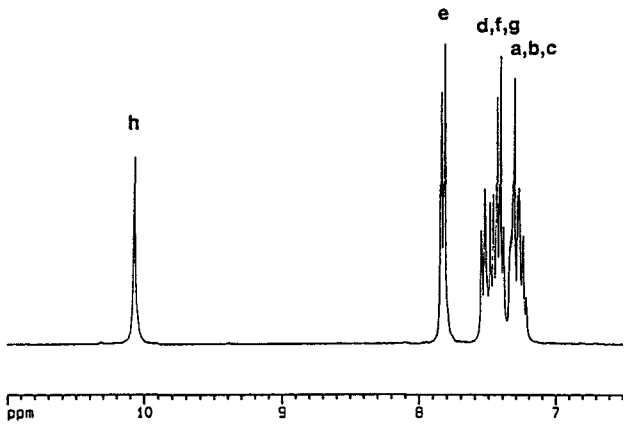
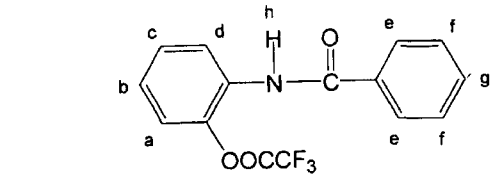


Figure 2. ^{1}H-NMR spectrum of *N*-(2-trifluoromethoxyphenyl) benzamide (FMB).



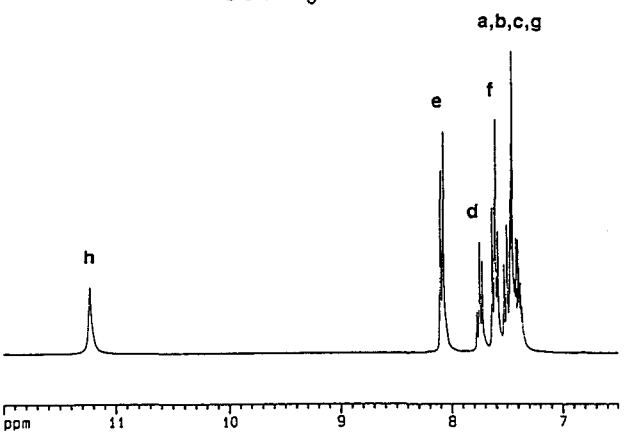


Figure 3. ^{1}H-NMR spectrum of 2-benzamidophenyl trifluoroacetate (BPF).

due to proton **a**. In the Figures 2 and 3, singlets at 10.1 and 11.3 ppm are due to the amide protons of FMB and BPF, respectively. For FMB and BPF, the peaks of the protons of the *N*-phenyl group have been shifted downfield because of the substitution of the hydroxy group. MPB and BPA show similar ^{1}H-NMR spectra. Table 1 shows the good agreement

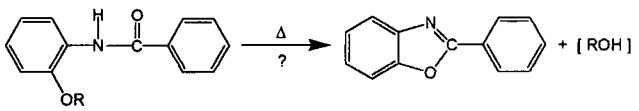
Table 1. Elemental analysis of model compounds

Samples	Calculated				Found			
	%C	%H	%N	%F	%C	%H	%N	%F
HPB	73.22	5.20	6.57		73.19	5.25	6.60	
FMB	59.79	3.58	4.98	20.27	59.61	3.53	4.97	19.8
BPF	58.26	3.26	4.53	18.43	58.07	3.19	4.54	18.0
MPB	73.99	5.77	6.16		73.80	5.70	6.14	
BPA	70.58	5.13	5.49		70.27	5.28	5.63	

between calculated and measured elemental compositions.

Cyclization Reaction in Model Compounds

PHA cyclizes at high temperature to form polybenzoxazoles (PBO) with the simultaneous release of water. To confirm that this cyclization can take place in the trifluoromethyl derivatized PHA, the model compound reaction was investigated. Scheme 3 represents the generalized cyclization reaction for the model compounds.



Scheme 3. Cyclization reaction expected for the model compounds during heating.

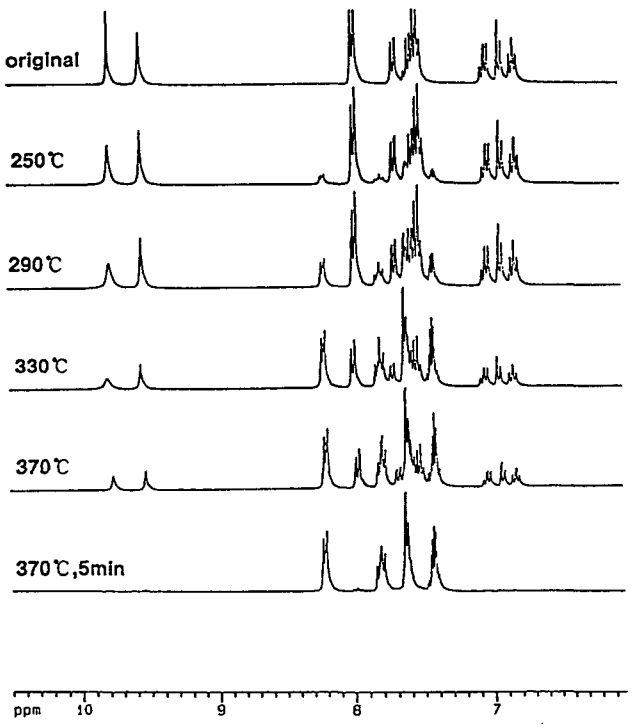


Figure 4. ^{1}H-NMR spectra of HPB heated at various temperatures.

In order to determine the proper heating conditions for cyclization, HPB was cyclized at various temperatures. Since HPB is volatile after melting, the cyclization reaction was conducted in a closed ampule. Figure 4 shows the ^{1}H-NMR spectra of HPB cyclized at 250, 290, 330, and 370 °C for 1 min. As shown in Figure 4, cyclization increased continuously with higher temperature and reached 66.6 % at 370 °C. However, if the time was extended at 370 °C for 5 min, almost all the hydroxyl group was lost and essentially complete cyclization was observed. Hence, we examined the cyclization reaction of model compounds at 370 °C for 5 min which should ensure sufficient time for cyclization conditions.

In case of FMB, which was heated to 370 °C and kept there for 5 min in sealed ampules, the ^{1}H-NMR showed no change from the starting NMR in Figure 2. This means that FMB did not cyclize on heating. On the other hand, as shown in Figure 5, the ^{1}H-NMR spectra of BPF heated at 370 °C for 5 min showed no amide proton peak. The ^{19}F-NMR spectrum of the same sample showed no fluorine peak. These results mean that trifluoromethyl ester type derivative can cyclize readily on heating, while the trifluoromethyl ether type cannot. We obtained similar results for the methyl ether and methyl ester group containing model compunds. MPB showed the same ^{1}H-NMR spectrum before and after

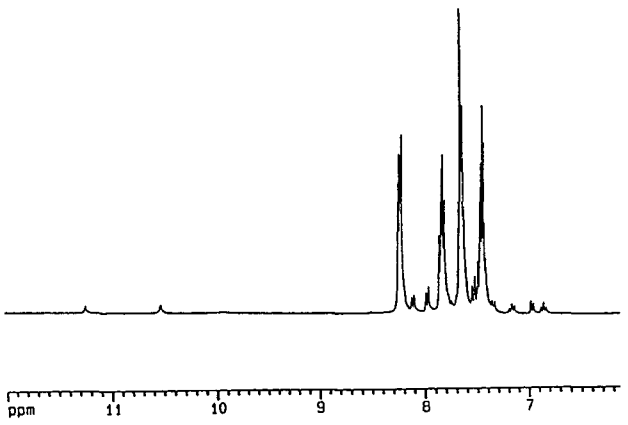
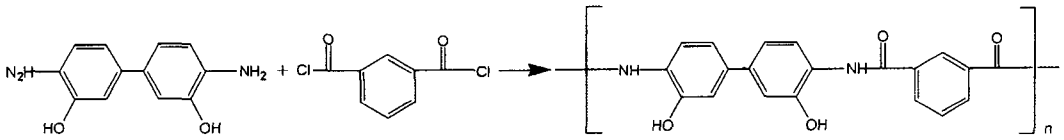


Figure 5 ^{1}H-NMR spectrum of BPF after cyclization at 370 °C for 5 min.



Scheme 4. Synthesis of PHA from 3,3'-dihydroxybenzidine and isophthaloyl chloride.

heating. On the other hand the ester, BPA showed no amide and methyl peaks after heating. This means that methyl ester derivative can cyclize on heating, while the methyl ether derivative cannot. In Scheme 3, for a model compound to cyclize, the R group should come off the oxygen after the ether oxygen attacks the carbonyl carbon in a nucleophilic displacement. However, the O-R bond is thought to be too strong to be ruptured, which would prevent the cyclization reaction during heating.

Properties of Derivatized PHA

The low temperature solution polymerization technique was used to synthesize polyhydroxyamide according to the method reported previously[1]. Scheme 4 represents the synthesis of PHA from 3,3'-dihydroxybenzidine and isophthaloyl chloride.

The intrinsic viscosity of PHA synthesized in this study is 1.40 d*l*/g. As can be seen in the previous section, the ester derivatives can cyclize on heating. Hence, we have tried to introduce the trifluoromethyl ester pendant group on the hydroxyl group. However, the acylation of the hydroxyl group in the polyhydroxyamide was much more difficult than the acylation of HPB. Even though 4-pyrrolidinopyridine was a very effective catalyst for the acylation of HPB, we could not obtain the completely derivatized PHA by using 4-pyrrolidinopyridine. Hence, we have made two samples with different degrees of derivatization, i.e., 91 % (sample P-0.91) and 58 % (sample P-0.58), and compared the properties with underivatized PHA (sample P-0). Samples P-0.58 and P-0.91 were obtained by derivatizing sample P-0 with trifluoromethyl acetate according to the method mentioned in the experimental section.

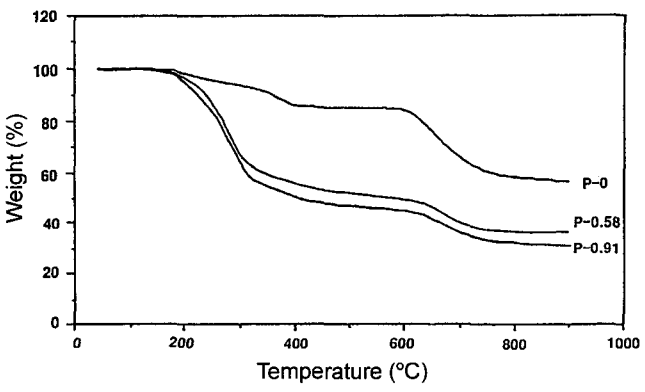


Figure 6. TGA thermograms of trifluoromethyl derivatized PHA.

Table 2. Observed and calculated char yields of PHA and its derivatives

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

[a]%Substitution of trifluoromethyl group calculated from ^{1}H-NMR data.
[b]Char yield read directly from the TGA thermograms at 900 °C.
[c]Char yield calculated between 500 °C and 900 °C, when making correction for the weight lost during cyclization.

Figure 6 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 Figure 6, the weight loss due to cyclization increases with degree of derivatization because of the higher molecular weight of trifluoroacetic acid than water. If we assume 100 % cyclization, the weight loss of each sample should be as follows: 10.4 % for P-0, 23.8 % for P-0.58, and 39.5 % for P-0.91. However, all the samples show higher weight loss than the theoretical value. This implies that there must have been an elimination of molecules other than trifluoroacetic acid and water in this temperature range. The char yield is sometimes used as an indication of flammability of a polymer. Since the PHA and its derivatives 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 2 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 polybenzoxazoles formed after cyclization have similar thermal stability.

Conclusions

The trifluoromethyl or methyl ester group containing model compounds can cyclize during heating. On the other hand, the trifluoromethyl or methyl ether containing model

compounds cannot cyclize on heating. The O-R bond is thought to be too strong to be ruptured, which would prevent the cyclization reaction during heating.

The trifluoromethyl ester containg PHA shows nearly same 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 nearly same thermal stability as the underivatized PHA after cyclization.

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