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Thermal cyclodehydration of aromatic precursor polymers to polybenzoxazole and polyimide; their thermal and mechanical properties

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Summary

Two precursor polymers, polyhydroxyamide (PHA) and poly(amic acid) (PAA) for polybenzoxazole (PBO) and polyimide (PI), respectively, showed large endothermic enthalpies (ΔH) in DSC thermograms. The values of enthalpy become smaller, and then unobservable with increasing cyclodehydration. The cyclization onset temperature (T_1) of the PHA and PAA occurred at 255-309 °C and 175-234 °C, respectively. Of the two precursor polymers, T_1 showed an increase with increasing cyclodehydration. The initial decomposition temperature (T_2) showed no significant change dependent on cyclodehydration. The tensile properties of the two precursors were enhanced drastically with increasing degree of cyclodehydration. PHA was shown to have excellent solubility only in strong acids at room temperature. In contrast, PAA was soluble in all the testing solvents at room temperature.

Introduction

Aromatic polybenzoxazoles[1-3] (PBO) and polyimides[4,5] (PI) comprise a class of heterocyclic polymers that exhibits outstanding thermo-oxidative stability, high tensile modulus and strength, and superior chemical resistance. While these materials possess thermal and mechanical properties far superior to partially aromatic systems, they require further improvements in the area of processability. This problem of processing is currently being examined through the following approaches, often used in combination[6,7]: random copolymerization, inclusion of flexible moiety and/or kinks in the main polymer chain and introduction of precursor polymers.

Recently, several research groups have been formed to search for both good solubility in several organic solvents and also processable heterocyclic polymers in the precursor states[5,8]. Compared with heterocyclized polymers, PBO and PI, precursor polymers have greater solubility and processability. Also, they can adsorb large amounts of heat energy, and release flame quenching molecules, such as water, in the cyclization

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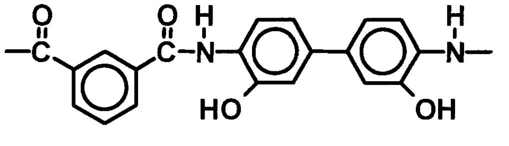
process[9-11].

In this paper, we discuss the characterizations of two wholly aromatic precursor polymers which have rigid biphenyl rings with amide linkages. These polymers are polyhydroxyamide (PHA), precursor to polybenzoxazole (PBO), and poly(amic acid) (PAA), precursor to polyimide (PI). The thermal behavior, mechanical property, degree of crystallinity, and solubility of the PHA films were compared with those of films processed from the PAA as a function of degree of cyclodehydration.

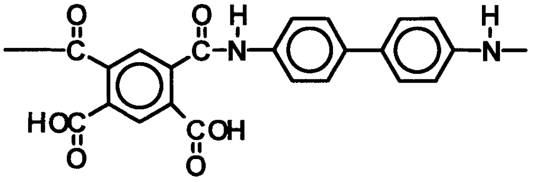
Experimental

Preparation of precursor polymers

PHA and PAA were prepared in N,N-dimethyl acetamide (DMAc) with a conventional solution polymerization[8]; PHA was synthesized with 3,3'-dihydroxybenzidine and isophthaloyl dichloride, and PAA was obtained from pyromellitic dianhydride and benzidine. The chemical structures of the two precursors are as follows:



PHA



PAA

The inherent viscosities of the two precursors were measured at 30 °C by using 0.2g/dL solution in DMAc. These inherent viscosities of the PHA and PAA were 1.20 and 1.28, respectively.

Film preparation

The synthesized polymer solution was cast on glass slides and then dried in vacuum at 40-50 °C for one day. The films were then cleaned in an ultrasonic cleaner 5 times, for 30 minutes each time to remove the residual DMAc in the precursor films. These films with solvent removed were dried again in a vacuum oven at 40-50 °C for one day. The films were approximately 10-15 µm in thickness.

Characterization

A DuPont 910 differential scanning calorimeter (DSC) equipped with a DuPont 910 thermogravimetric analyzer (TGA) was used to determine the thermal transitions under a nitrogen atmosphere; the heating rate was 20 °C /min.

The wide-angle X-ray diffraction patterns were obtaind on a Rigaku (B/Max. 2500V) X-ray diffractometer, using Ni-filtered Cu-Kα radiation. The scanning rate was 4°/min over a range of 2θ=5-50°. Degree of crystallinity was calculated from the reflection areas of the crystalline and amorphous diffractions.

Mechanical tensile properties were investigated using on a tensile tester (Instron Mechanical Tester, model No. 5564) with a crosshead speed of 5mm/min. Average values of more than six measurements were taken for each sample.

Degree of cyclodehydration

To get information about degree of cyclodehydration, the precursors were isothermally cyclized in TGA for a chosen time in the temperature ranges of 250-450°C and 100-250°C for PHA and PAA, respectively. Degree of cyclodehydration was obtained from the experimental data from TGA curves with calculated weight loss for cyclization. There is a good correlation between the calculated and experimental weight losses, indicating that all the water is driven off and essentially complete cyclization is obtainable.

Results and discussion

Thermal behavior

The thermal properties of the PHA and PAA were evaluated by means of DSC and TGA. Some of these DSC data are listed in Table 1. The minimum points of PHA

Table 1. Properties of PHA and PAA at different degree of cyclodehydrations

PHA				PAA			
D. CH.[a] %	T[b] °C	ΔH[c] J/g	D.C.[d] %	D. CH. %	T °C	Δ H J/g	D.C. %
0	319	221.1	0	0	164	213.8	0
45	319	131.7	8	65	195	21.8	27
80	351	8.4	13	85	202	0.4	39
100	n.o.[e]	n.o.	22	100	n.o.	n.o.	43

[a] Degree of cyclodehydration [b] Minimum point in endothermic curve.
[c] Endothermic enthalpy. [d] Degree of crystallinity. [e] Not observed.

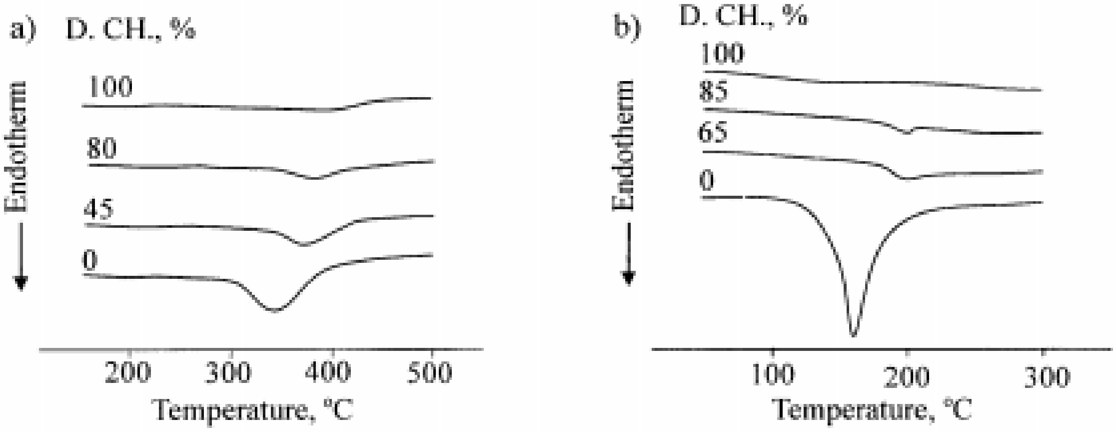


Figure 1. DSC thermograms of a) PHA and b) PAA before and after cyclodehydration.

endothermic peaks were in the range of 319-351 °C, while those of PAA were 164-202 °C, dependent on degree of cyclodehydration. The endothermic enthalpies (ΔH) of the two precursors were much larger than those of other thermoplastic polymers; 221.1 for PHA and 213.8 J/g for PAA, respectively. They were shown to possess heat capacities from 221.1 to 8.4 J/g and from 213.8 to 0.4 J/g with increasing degree of cyclodehydration in PHA and PAA, respectively. ΔH of the two precursors was diminished drastically with increasing degree of cyclodehydration. Finally it is shown that there is no endothermic peak in DSC thermograms PHA and PAA at complete cyclodehydration as shown in Figure 1.

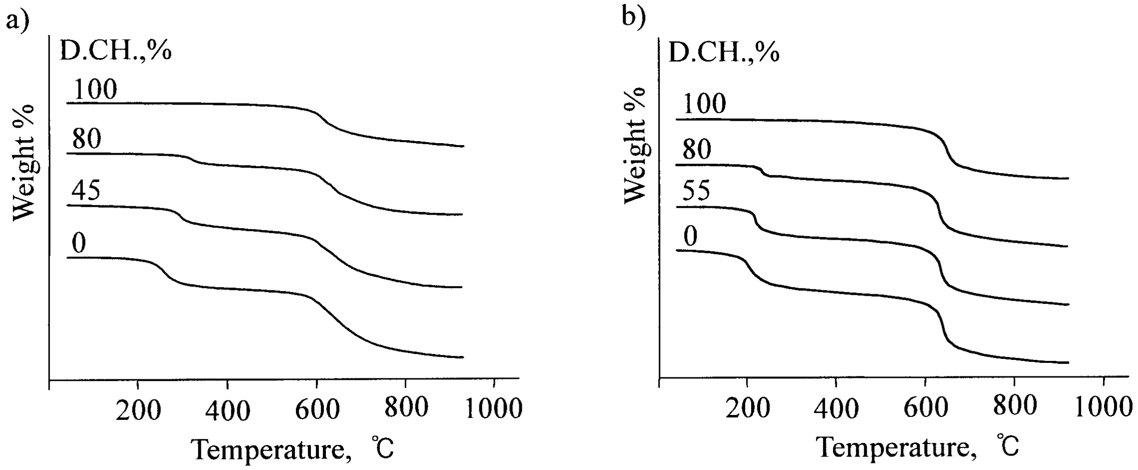


Figure 2. TGA thermograms of a) PHA and b) PAA before and after cyclodehydration.

Table 2. TGA analyses of PHA and PAA at different degree of cyclodehydrations

PHA					PAA				
D. CH.[a] %	T_1[b] °C	Wt. Red.[c] %	T_2[d] °C	Wt^R_{900}[e] %	D. CH. %	T_1 °C	Wt. Red.[f] %	T_2 °C	Wt^R_{900} %
0	255	11(10)[g]	577	45	0	175	9(9)	584	46
35	282	7	575	57	35	189	6	586	56
45	305	5	577	60	55	219	4	589	61
80	309	2	579	75	80	234	2	590	61
100	-	0	578	75	100	-	0	590	65

[a] Degree of cyclodehydration. [b] 1st weight reduction onset temperature.

[c] Weight reduction between 250°C and 400 °C in TGA thermogram.

[d] 2nd weight reduction onset temperature. [e] Weight percent of residue at 900 °C.

[f] Weight reduction between 100 and 250 ℃ in TGA thermogram.

[g] Values in parentheses represent calculated values.

The minimum points in the endothermic curve and the values of ΔH for PHA were higher that those for PAA, although their inherent viscosities were not considerably different. This can be attributed to the difference of the two polymer structures. These precursors were obtained through two step weight reductions with increasing temperature. First step (T_1) is associated with the conversion to cyclized polymers via dehydration, e.g. PBO and PI. Second (T_2) is thermal decomposition caused to char formation[12]. Figures 2(a) and (b) show TGA curves of the two polymers at different degree of cyclodehydration. T_1 values of the PHA and PAA were observed at 255-309 °C and 175-234 °C, respectively, depending on cyclization(see Table2). For both precursor polymers, T_1 is likely to increase with increasing degree of cyclodehydration.

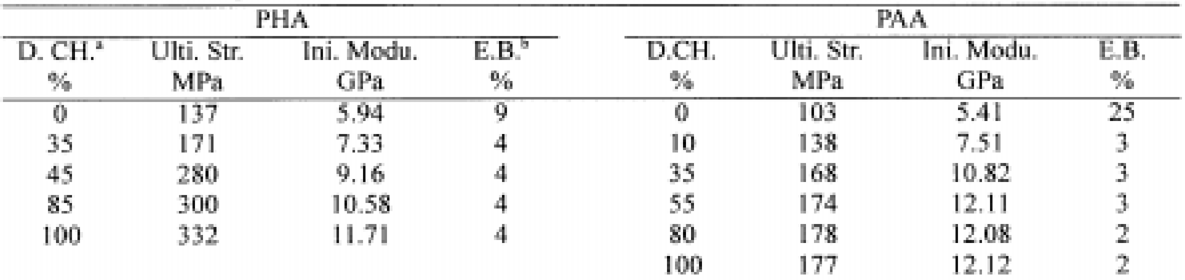
The theoretical weight losses of PHA and PAA by cyclization (PBO and PI formations) are 10 and 9 %, respectively, and these values agree with the experimental values (see Table 2). The values of the weight loss due to loss of water decreased remarkably with increasing degree of cyclization in the two samples.

Initial decomposition temperature, T_2, did not change significantly depending on cyclization. T_2 of the PHA and PAA were observed in the temperature range of 575-579 °C and 584-590 °C, respectively. These TGA results confirm that the two samples are fairly thermally stable compared to other thermoplastic polymers. Weight residues at 900 °C of the PHA were in the range of 45-75% with increasing degree of cyclodehydration. The higher wt% residue is thought to be the result of char formation in combustion. A similar trend was observed for the PAA.

Mechanical property

The tensile properties of the PHA and PAA films are summarized in Table 3. The tensile properties of the two precursors were enhanced drastically by increasing cyclodehydration. With increasing degree of cyclodehydration from 35 to 100% (PBO), the values of the ultimate strength and initial modulus for PHA increased linearly from 137 to 332 MPa and 5.94 to 11.71 GPa, respectively. In particular, the ultimate strength of PBO is more twice than that of the uncyclized precursor.

Table 3. Tensile properties of PHA and PAA at different degree of cyclodehydrations



PHA				PAA			
D. CH.[a] %	Ulti. Str. MPa	Ini. Modu. GPa	E.B.[b] %	D.CH. %	Ulti. Str. MPa	Ini. Modu. GPa	E.B. %
0	137	5.94	9	0	103	5.41	25
35	171	7.33	4	10	138	7.51	3
45	280	9.16	4	35	168	10.82	3
85	300	10.58	4	55	174	12.11	3
100	332	11.71	4	80	178	12.08	2
				100	177	12.12	2

[a] Degree of cyclodehydration. [b] Elongation at break.

Similar trends were observed in PAA. As shown in Table 3, the strength and modulus values increased from 103 to 177 MPa and 5.41 to 12.12 GPa, respectively, with increasing degree of cyclization.

The elongation percentages for break at cyclization polymers were 2-3%. These held constant values regardless of degree of cyclodehydration.

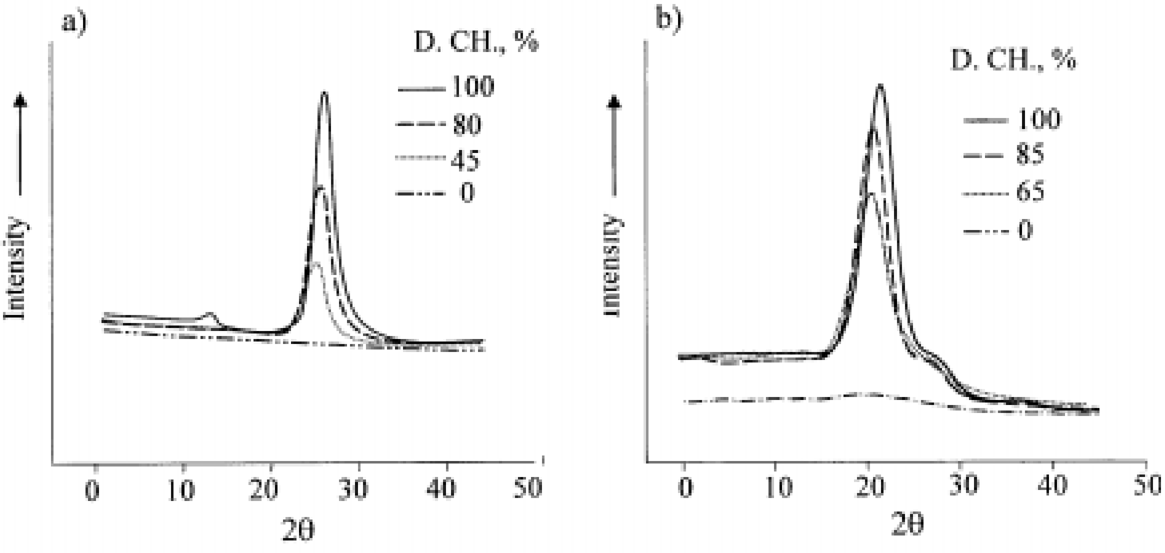


Figure 3. Wide angle X-ray diffractograms of a) PHA and b) PAA before and after cyclodehydration.

Degree of crystallinity

Figure 3 shows the diffractogram for the PHA and PAA with increasing degree of cyclodehydration. For two samples showed amorphous diffration patterns in precursor state. However, when cyclodehydrations increased to the range of 45 to 80%, a strong peak was observed at 2θ=26° for PHA, In particular, the sample completely cyclized showed a sharp peak at 2θ=26° and a new small peak appeared at 2θ=14 °. As shown in Table 1, the degree of crystallinity of PHA increased from 0 to 22% with increasing cyclodehydration.

One strong peak was observed at 2θ=20 ° and a broad peak, 2θ=29 ° was observed for 65% cyclized PAA. When degree of cyclodehydration increased from 65 to 100% , the more strong peak shifted to the higher 2θ=22 °. Also, the degree of crystallinity of PAA increased from 0 to 43% with increasing cyclodehydration.

Solubility

The solubility tests of the two precursors are shown in Table 4. PHA was revealed to have excellent solubility at room temperature in strong acids such as chlorosulfonic acid (Cl-SA), methansulfonic acid (MSA), and sulfuric acid. PHA was also soluble in DMAc and NMP with 0.1-0.5 wt% of LiCl above 80 °C, but was not soluble at all in DMSO at room temperature. On the contrary, PAA was soluble in all the testing solvents at room temperature as shown in Table 4. However, the two precursors are usually insoluble in common solvents; acetone, ether, chloroform and alcohols et al.

Solubility was significantly decreased with increasing degree of cyclodehydration. The main reason for the poor solubility is that cyclization reaction of the precursor facilitates a more rigid polymer structure, which was confirmed by DSC,

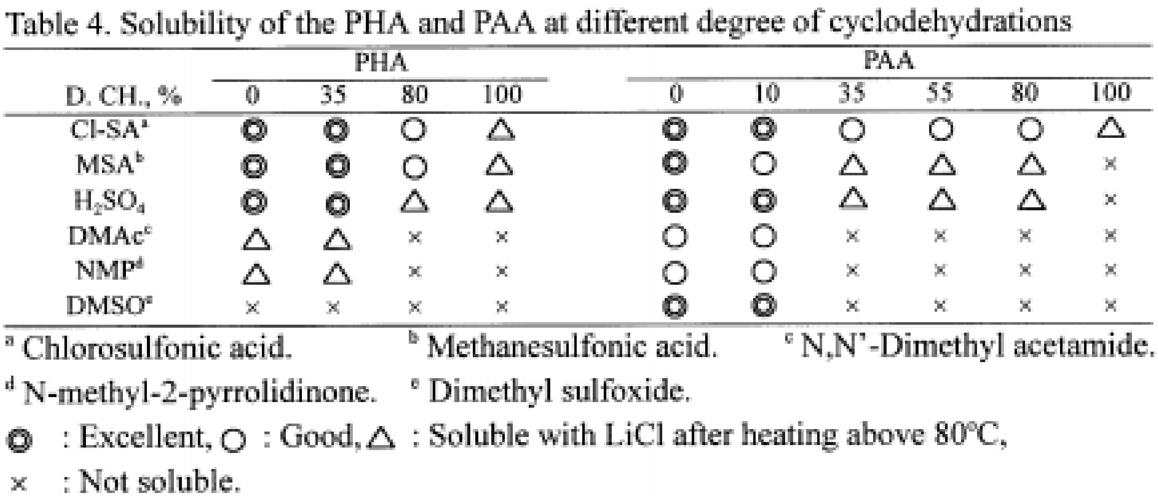


Table 4. Solubility of the PHA and PAA at different degree of cyclodehydrations

	PHA				PAA					
D. CH., %	0	35	80	100	0	10	35	55	80	100
Cl-SA[a]	◎	◎	○	△	◎	◎	○	○	○	△
MSA[b]	◎	◎	○	△	◎	○	△	△	△	×
H_2SO_4	◎	◎	△	△	◎	◎	△	△	△	×
DMAc[c]	△	△	×	×	○	○	×	×	×	×
NMP[d]	△	△	×	×	○	○	×	×	×	×
DMSO[e]	×	×	×	×	◎	◎	×	×	×	×

[a] Chlorosulfonic acid. [b] Methanesulfonic acid. [c] N,N'-Dimethyl acetamide.

[d] N-methyl-2-pyrrolidinone. [e] Dimethyl sulfoxide.

◎ : Excellent, ○ : Good, △ : Soluble with LiCl after heating above 80°C,

× : Not soluble.

TGA, and X-ray data.

Conclusions

The two precursors are fairly thermally stable in nitrogen and show unusually large heat capacities when compared with other thermoplastic polymers. As a whole, thermal and tensile property were enhanced remarkably with increasing degree of cyclodehydration. In contrast, cyclized polymer showed significantly decreased solubility when compared with their corresponding uncyclized precursors. Degree of crystallinity of the two samples was increased linearly with increased cyclodehydration. These X-ray results are also in agreement with the thermo-mechanical property results.

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