폴리히드록시아미드와 그 치환체의 고리화 반응(I)

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Thermal Cyclization of Aromatic Polyhydroxyamides and its Derivatives(I)

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1. Introduction

Wholly aromatic polybenzoxazoles(PBO) are well established as high performance materials with excellent thermal stability and mechanical properties. Heterocyclic precursor polymers such as polyhydroxyamides(PHA) have been interested in the field of high performance flame retardant polymers.[1]

Precusor polymers have the advantages that they are easier to process, don't require strong solvents and can adsorb large amounts of heat energy during the cyclization process. Thus, if these materials are used in the uncyclized form, they will have increased heat capacity, and when cyclized they will liberate water or a flame retardant, depending upon the design of the chemical groups undergoing the cyclization. Hence, the precusor will be converted to a high temperature heterocyclic polymer possibly containing a flame retardant, and will consume a considerable amount of energy in the process.[2,3]

The PHAs can be converted to PBOs when ignited. 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. In the case of the hydroxyl groups of PHA are derivatized with alkyl compounds, they may act as more effective extinguishers under flame conditions.

In the present study, we have synthesized the PHA and the PHA derivatives containing alkyl ester groups and investigated the cyclization chemistry of them.

2. Experimental

2.1 Materials

3,3'-dihydroxybenzidine(DHB) was obtained TCI America, and the chemicals were purified before use. Isophthaloyl chloride(IPC), acetic anhydride, propionic anhydride, butyric anhydride, isobutyric anhydride and 4-pyprroldinopyridine were obtained from Aldrich Chemical Company. N,N-dimethylacetamide(DMAc) was selected for solvents.

2.2. Synthesis of polyhydroxyamide.

DHB was dissolved in anhydrous DMAc. The solution was cooled to 0℃, and IPC dissolved in DMAc are added dropwise with stirring. The solution was stirred for 1 hour at 0℃, 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 40℃ for 48 hours.

2.3 Derivatization of polyhydroxyamide

PHA were derivatized with acetic anhydride, propionic anhydride, butyric anhydride and isobutyric anhydride. PHA and 4-pyrrolidinopyridine were dissolved in DMAc. Then acetic anhydride, propionic anhydride, butyric anhydride and isobutyric anhydride were added dropwise at room temperature. After 3 hours, the reaction mixture was poured into water with stirring, and derivatized polymers were filtered and dried in vacuum at 40℃ for 48 hours.

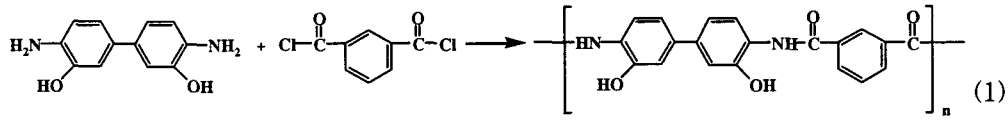
2.4 Characterization of PHA and derivatized PHA

The structural analyses of PHA and derivatized PHA were performed by ^{1}H-NMR spectroscopy using a Unity Inova 400 NMR spectrometer on a DMSO-d_6 solution. The thermal analysis performed by TA Instrument DSC 2910, Perkin Elmer DSC-4 and Perkin Elmer TGA-7 under N_2 atmosphere with a heating rate of 20℃/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 synthesis of PHA.



(1)

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 alkyl ester pendent group on hydroxyl group. Scheme (2) represents the generalized equation for the synthesis of derivatized PHA.

(2)

R=CH_3(PAA), CH_2CH_3(PPA), $CH_2CH_2CH_3$(PBA), $CH(CH_3)$(PIBA)

3.3 Characterization

Figure 1 shows the TGA thermograms of PHA and derivatized PHA. Each TGA thermogram shows the typical two-step weight loss during heating.

3.4 Cyclization of PHA and derivatized PHA

Cyclization behaviors of PHA and derivatized PHA were examined by using DSC. The peak area was decreased with increasing temperature, which indicated that endothermic peak was due to cyclization reaction.

The effect of time and temperature on degree of cyclization was measured by means of DSC.

4. Conclusion

The hydroxyl groups of PHA could be substitued with acetic anhydride, propionic anhydride, butyric anhydride and isobutyric anhydride with the aid of the catalyst such as PLP in DMAc. Cyclization behaviors of PHA and the derivatized PHA were examined by using DSC. We could find that derivatized PHA was cyclized at lower temperature than PHA and the cyclization reaction of derivatives was faster than that of the PHA

5. Reference

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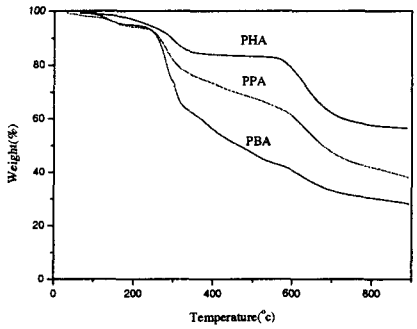

Figure 1. TGA thermograms of PHA and derivatized PHA