

PHA 및 그 유도체의 열적 고리화 거동 고리화 거동(I) - 모델화합물 연구 -

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Thermal Cyclization of PHA and its Derivatives(I) - Model compound study -

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1. Introduction

Aromatic polybenzoxazoles(PBOs) display excellent thermal stability plus good solvent and chemical resistance. Wholly aromatic PBOs, in fact, are soluble only in strong acids(e.g., sulfuric, methanesulfonic, triflic, and polyphosphoric acids).¹ However, fully heterocyclized polymers have shown some drawbacks in solubility and processing. This problem of processing is currently being exploited to obtain unusual combinations of physical properties in fibers and films.

Many researchers have examined the possibility of heterocyclic precursor polymers that can be used as high performance, fire-retardant films, composites and fibers. Precursor polymers have the advantages that they are easier to process, do not require strong solvents and can adsorb large amount 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.²

The goal of this study is to focus on the development of the derivatives of polyhydroxyamides having good thermal stability and fast cyclization kinetics at relatively low temperature.³

2. Experimental

2.1 Materials

o-aminophenol, benzoyl chloride, acetic anhydride, butyric anhydride,

isobutyric anhydride were obtained from Aldrich Chemical Company. N,N-dimethylacetamide(DMAc), N,M-dimethylformamide(DMF) were selected for solvents.

2.2. Synthesis of the model compound

Synthesis of N-(2-hydroxyphenyl)benzamide

N-(2-hydroxyphenyl)benzamide(HPB) was prepared by the reaction of *o*-aminophenol with benzoyl chloride in DMAc. A solution of *o*-aminophenol(2.13g, 0.01mol) in DMAc 50ml was cooled with an ice-water bath and was stirred at 0°C. To this solution was added with stirring benzoyl chloride(1.02g, 0.01mol). The mixture was stirred at 0°C for 1 hour and at room temperature for 5hours. The precipitation was obtained by crystallization into water and dried in vacuum.

Synthesis of 2-benzamidophenyl acetate

2-benzamidophenyl acetate(BPA) was obtained by derivatizing HPB with butyric anhydride at room temperature in DMF. After 3 hours the mixture was poured into water and the precipitate was dried in vacuum.

Synthesis of 2-benzamidophenyl butanoate

2-benzamidophenyl butanoate(BPB) was obtained by derivatizing HPB with butyric anhydride at room temperature in DMF. After 6 hours the mixture was poured into water and the precipitate was dried in vacuum.

Synthesis of 2-benzamidophenyl isobutanoate

2-benzamidophenyl isobutanoate(BPI) was obtained by derivatizing HPB with isobutyric anhydride at room temperature in DMF. After 6 hours the mixture was poured into water and the precipitate was 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 200°C to 250°C for 30 and 60 min.

2.4 Characterization of the model compounds

The structural analyses of model compounds were performed by ¹H-NMR and FT-IR. The thermal analyses were performed by DSC 2910(TA Instruments) under N₂ atmosphere with a heating rate of 20°C/min.

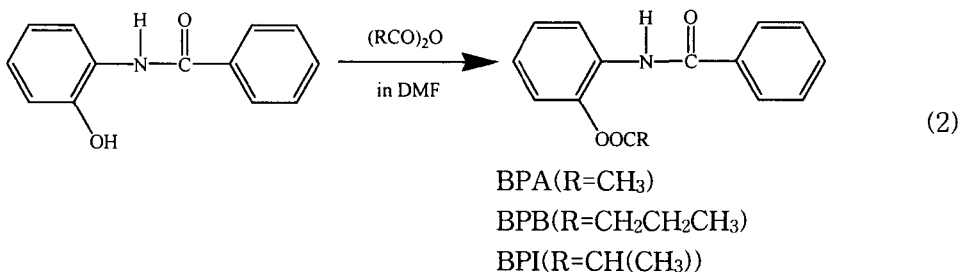
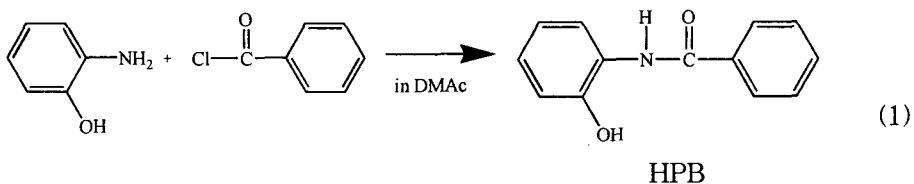
3. Results and Discussion

3.1. Synthesis of model compounds

Scheme (1) represents the synthesis of HPB. Scheme (2) is generalized equation for the derivatization of HPB.

3.2 Cyclization of model compounds

The cyclization of model compounds HPB, BPA, BPB and BPI were examined by IR.



The degree of cyclization was calculated by using NH peak area (3409cm⁻¹) in IR spectra. Benzene ring peak of benzoyl chloride was selected as a reference peak. The cyclization reaction was confirmed by ¹H-NMR and FTIR analysis. The kinetic study on the cyclization reaction was also conducted for the four model compounds.

4. Reference

- 1) G. L. Tullos and L. J. Mathiasi, *Macromolecules*, **32**, 3598-3612(1999).
- 2) J. H. Chang, M.J. Chen, *Polymer*, **39**, 5649-5654(1998)
- 3) Y. H. So and J. P. Heeschen, *J. Org. Chem.* **62**, 3552-3561(1997)