Synthesis of Cyclic Organic Molecules by the Self-Condensation of 2-Fluoro-4-Hydroxy Benzonitrile

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Introduction

Cyclic organic molecules have received an increasing attention due to their unique properties deriving from the topology. Various synthesis methods of cyclic molecules have been reported, however most of them consist of complicated multistep procedure [1]. In this work, we report an easy synthesis method of a cyclic organic molecule by the self-condensation of 2-fluoro-4-hydroxy benzonitrile.

Experiment

Poly (alylene ether nitrile)s (PENs) were synthesized by the self-condensation of 2-fluoro-4-hydroxy benzonitrile (**Scheme 1**). The polymerization was carried out in the presence of lithium hydroxide in NMP at 180 ^{o}C. The polymer was purified by preparative HPLC and column chromatography. The resulting polymer was analyzed by ^{1}H NMR, Viscotek triple detection SEC (TD-SEC) and MALDI-TOF mass measurements.

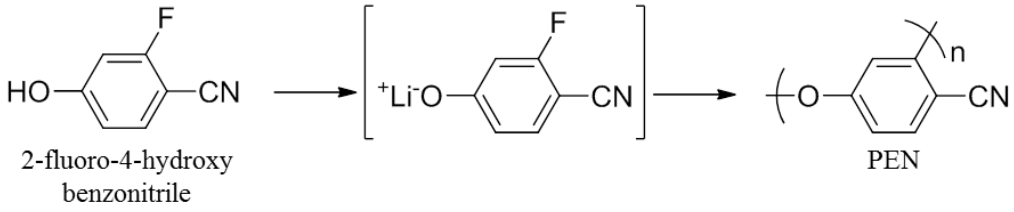
Results and Discussion

TD-SEC results (**Figure 1(a)**) suggest that the crude PENs after the polymerization contains at least two components with different molecular weight. The refractive index surface ratio suggests that the content of low molecular weight compound is approximately six times larger than that of high molecular weight compound, suggesting that low molecular weight compound is the main product. **Figrure 1 (b)** suggests that the low molecular weight compound was successfully separated by preparative HPLC and column chromatography. As shown in MALDI-TOF mass spectrum of the purified PENs (**Figure 2),** the peak at m/z = 490.60, which is assumed to be the adduct with Na^{+}, corresponds to PENs possessing the expected chemical structure with the degree of polymerization of 4; $(C_7H_3NO) \times 4$, plus Na^{+} = 491.39. Therefore, the peak was derived from cyclic PEN tetramer (**Scheme 2**).

In this research, 2-fluoro-4-hydroxy benzonitriles were used as AB type monomer, which has one reactive group of A type and one reactive group of B type at meta position. Therefore, this synthesis is easier to produce cyclic compounds. When PENs form cyclic shape, these compounds don't proceeded growth reaction. For reasons mentioned above, in this synthesis method, low molecular weight cyclic compounds are major compounds.

Reference

1) H. Oike, H. Imaizumi, T. Mouri, Y. Yshioka, A. Uchibori and Y. Tezuka, *J. Am. Chem. Soc.*, **122**, 9592 (2000)



Scheme 1. Synthesis of PENs

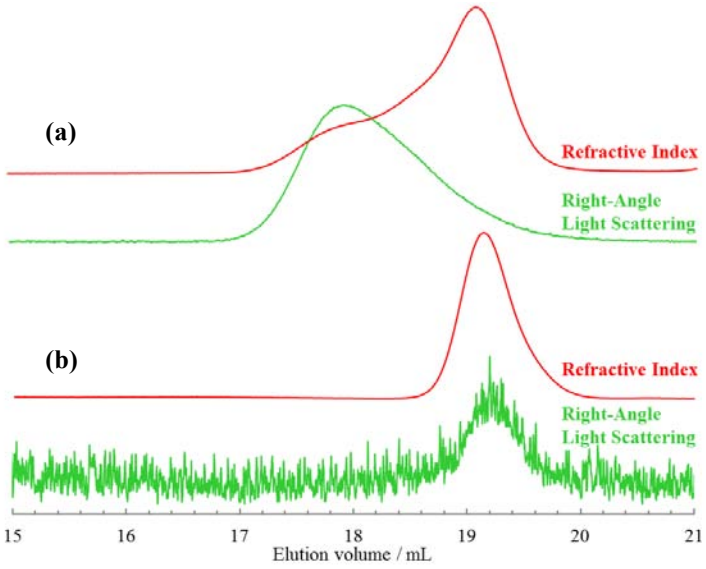


Figure 1. TD-SEC plofiles. (a)the crude PENs, (b)the purified PENs (left) and its enlarged one (right) (DMF containing 5.0 mM LiBr was used as eluent at late flow 0.6 mL/min, with TSK-GEL alpha-M × 2)

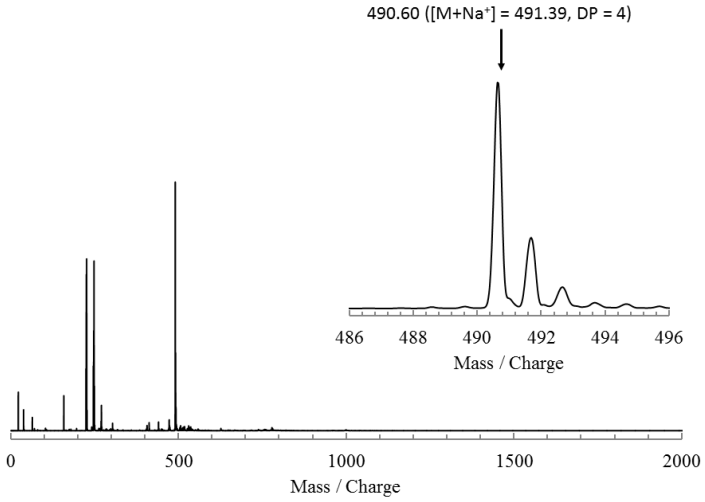
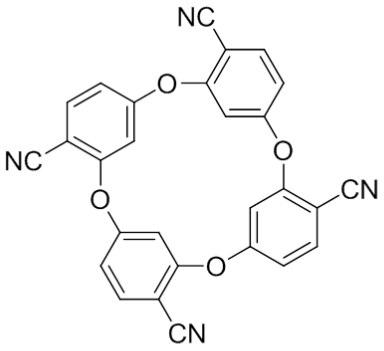


Figure 2. MALDI-TOF mass spectrum of purified PENs (bottom), and its expected one (top). (Linear mode, matrix: dithranol with sodium trifluoroacetate. DP denote the number of monomer units in the product.)



Scheme 2. Structure of Cyclic PEN Tetramer