

Preparation of aromatic polyesters by direct polymerization in the presence of boronic anhydride under non-stoichiometric condition



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ABSTRACT

Direct polymerizations of *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) in the presence of boronic anhydride were examined by using crystallization under non-stoichiometric condition. The polymerizations were carried out with the addition of monofunctional compounds such as an aromatic carboxylic acid and a phenol. High molecular weight poly(*p*-oxybenzoyl) (POB) and poly(2-oxy-6-naphthoyl) (PON) were obtained in the form of precipitates, and their molecular weights were much higher than those calculated according to the stoichiometric imbalance. Oligomers were formed by the direct polymerization with eliminating water in the solution, and then they were precipitated to form the crystals at the initial stage of the polymerization. Oligomers end-capped by monofunctional compounds were also formed in the solution, but the polymerization continued with the elimination of monofunctional compounds by the ester exchange reaction. The end-capped oligomers were precipitated in the middle of the polymerization, and the polymerization proceeded efficiently even in the precipitated crystals by not only the direct polymerization but also the ester exchange polymerization, resulting in the increase in molecular weight.

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1. Introduction

POB and PON attract a great deal of attention as high-performance polymers possessing many excellent properties such as mechanical property, thermal stability, chemical resistance and so on [1–5]. These aromatic polyesters are usually synthesized by the polymerization of the corresponding acetoxy aromatic acids with elimination of acetic acid. Although these polyesters are expected to be high-performance materials, they show neither fusibility nor solubility owing to their rigid structure, and the intractability makes them difficult to process by conventional procedures. In general, copolymerization is applied to give them the fusibility, and the aromatic copolyesters are well known as thermotropic liquid crystalline polymers. The whiskers of POB and PON had been prepared by using reaction-induced crystallization of oligomers, and they are expected as to be high-performance fillers [6–8]. This reaction-induced crystallization of oligomers during polymerization is a unique method to control the morphology of

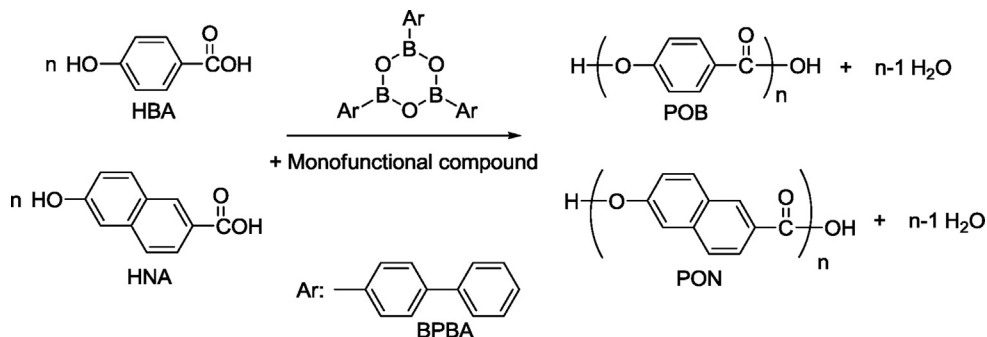
intractable polymers, because it cannot be limited by the intractability of polymers.

Direct synthesis of aromatic polyesters had also been developed as an elegant synthetic procedure, and numerous types of condensation reagents were developed so far [9]. These polymerizations are regarded as atom-economical syntheses and they will be widely accepted as environmental benign syntheses. It has been reported that the direct polymerization of HBA and HNA in the presence of anhydride of boronic acid such as 2,4,6-tri(biphenyl-4-yl)-1,3,5,2,4,6-trioxatriborinane (BPBA) shown in Scheme 1, gave the precipitates of POB and PON crystals having unique morphology [10,11]. In these polymerizations, BPBA activates the carboxyl group to react with the phenolic hydroxyl group in liquid phase. Even though the oligomers were precipitated from the solution to form the crystals, the polymerization occurred in the precipitated crystals to yield high molecular weight polymers.

It is well known that stoichiometric balance between two reactive groups is of the greatest importance to synthesize high molecular weight polymers by the step-growth polymerization [12]. If the polymerization is carried out in homogeneous system under non-stoichiometric condition, it is usually terminated and the molecular weight becomes lowered according to the following equation (1).

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Scheme 1. Synthesis of POB and PON by direct polymerization of HBA and HNA in the presence of BPBA.

$$DP_n = \frac{1 + (N_1/N_0)}{(1-p) + (N_1/N_0)} \quad (1)$$

where, DP_n : number-average degree of polymerization, N_0 : number of monomers, N_1 : number of monofunctional compounds, p : extent of reaction

Several unusual polymerizations which did not obey the equation (1) had been reported and high molecular weight polymers were obtained even under non-stoichiometric condition [13–20]. These unique polymerizations can be categorized into two groups chemically and physically based on the mechanism, of which one is attributed to the drastic change in the reactivity of functional groups and another is attributed to the heterogeneous reaction field. In the latter case, heterogeneous polymerization in which the polymerization proceeds with precipitation yields polymers having higher molecular weights than the theoretically calculated values even though the reactivity of functional groups does not change during polymerization. The direct polymerizations of HBA and HNA in the presence of boronic anhydride are heterogeneous polymerizations as aforesaid, and they will be expected to afford high molecular weight polymers even under non-stoichiometric condition.

In this study, the polymerization of HBA and HNA in the presence of boronic anhydride was examined with the addition of monofunctional compounds such as an aromatic carboxylic acid and a phenol to clarify the influence of stoichiometric imbalance on molecular weight of POB and PON.

2. Experimental

2.1. Materials

HBA and HNA were purchased from TCI Co. Ltd. and recrystallized from a mixture of water and methanol. 4-Biphenylboronic acid (BPB) was purchased from Sigma–Aldrich Co. Ltd. and recrystallized from toluene. It has been reported that BPB undergo

dehydration upon simple heating to be converted into anhydrides, BPBA [21–23]. BPB was converted into BPBA during the purification by recrystallization as confirmed by IR spectroscopy. *p*-Hexyloxybenzoic acid (HOBA), 4-(4-hexyloxybenzyloxy)benzoic acid (HBBA) and *p*-hexyloxyphenol (HOPH) were synthesized according to the previously reported procedures [16,19]. 4-(4-Hexyloxyphenoxy)phenol (HPCP) was synthesized according to the previously reported procedure [24]. An isomeric mixture of dibenzyltoluene was obtained from Matsumura Oil Co. Ltd. (trade name: Barrel Therm 400, molecular weight: 380, boiling point: 382 °C) and distilled under reduced pressure (170–175 °C/0.3 mmHg).

2.2. Measurements

Morphology was observed on a HITACHI S-3500N scanning electron microscope (SEM). Samples were dried, sputtered with platinum–palladium and observed at 20 kV. Infrared (IR) spectrum was measured on a JASCO FT/IR-410 spectrometer. Wide angle X-ray scattering (WAXS) was performed on a Rigaku Geigerflex with nickel-filtered $CuK\alpha$ radiation (35 kV, 20 mA). Number-average degree of polymerization (DP_n) was determined by the end-group analysis using FT-IR and HPLC after hydrolysis according to the previous procedures [6,12,15].

2.3. Polymerization

A polymerization of HBA with HOBA in the presence of BPBA at χ_{HOBA} of 20 mol% is described as a typical procedure.

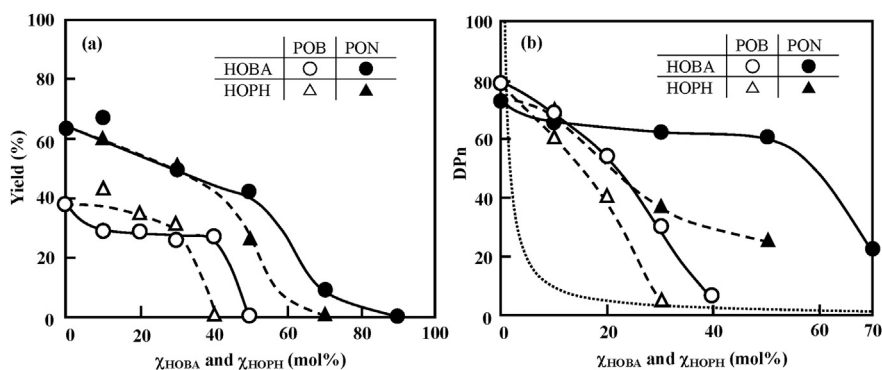


Fig. 1. Plots of (a) yield and (b) DP_n of precipitated POB and PON as a function of χ_{HOBA} (○, ●) and χ_{HOPH} (△, ▲). Polymerizations were carried out for 24 h. Dashed line in (b) is a curve calculated by eq. (1).

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