POLY(P-BENZAMIDE) OF MODERATE MOLECULAR WEIGHT BY YAMAZAKI PHOSPHORYLATION REACTION

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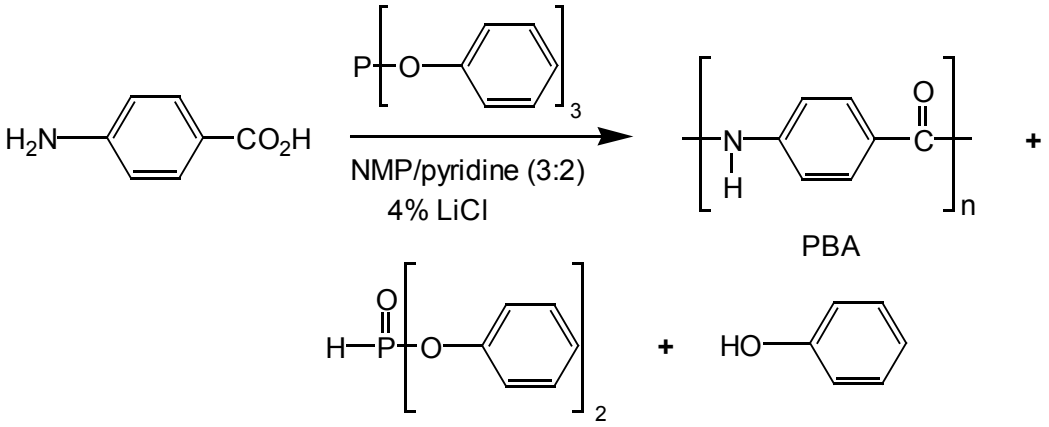


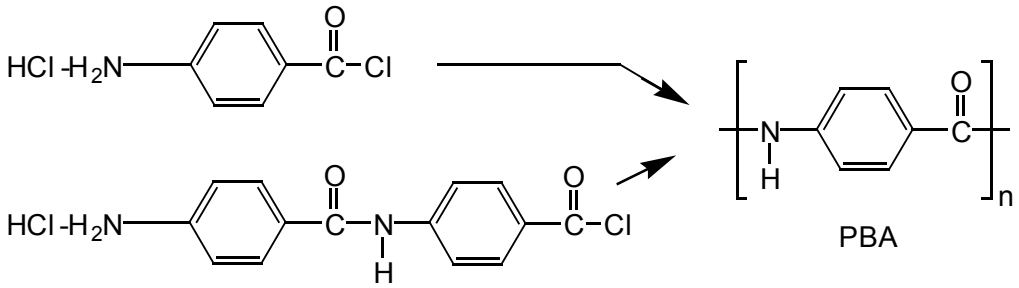
This type of reaction was first described by Yamazaki, et al,[5] and the reaction conditions were modified by Preston and Hofferbert.[6]

1. Procedure

A dry 250 ml three-neck conical flask is placed in a constant temperature oil bath (Note 1). The flask is fitted with a condenser, mechanical stirrer (Note 2) and an inlet and outlet for nitrogen gas. To remove air and traces of moisture, the flask is flushed with a stream of nitrogen dried by passing through a 20 cm column of Fisher G-16 mesh S-160 silica gel. To this prepared vessel are added *p*-aminobenzoic acid (2.743 g, 0.02 mole), 20 ml of N-methyl-2-pyrrolidone (NMP) containing 4% LiCl, 20 ml of pyridine, and triphenylphosphite (5.25 ml, 0.02 mol, Note 3). The oil bath is heated to 100°C, and this temperature is maintained for 3 hours. Poly(*p*-benzamide), PBA, is isolated by pouring the very viscous solution into rapidly stirring methanol in a blender jar. The polymer is washed in the blender with three 200 ml portions of methanol, and refluxed with 200 ml of methanol for 1 hour. After drying in a vacuum oven at 60°C to constant weight, the yield of polymer is nearly quantitative. The inherent viscosity of the polymer is 1.7 ± 0.2 dl/g (Note 4). PBA does not melt below 500°C. Polymer having inherent viscosity 1.5 to 1.6 dl/g forms a nematic phase at a concentration of 10.7 g/dl in dimethylacetamide containing 3% LiCl (Note 5).

2. Methods of Preparation

Poly(*p*-benzamide), PBA, of high molecular weight (0_{inh} $ 3.5 dl/g) can be prepared by the use of acid chloride monomers:[7,8]



PBA of higher molecular weight (0_{inh} = 2.4 to 3.0 dl/g) can be obtained by using reaction conditions similar to those described here, but employing as monomer 4,N-(4ℕ-aminobenzamido)benzoic acid.[9,10]

3. Notes

1. The Techne TE-7/P oil bath, which maintains the temperature within ± 0.5°C, is very suitable. The polycondensation can also be performed in a boiling water bath as described by Preston and Hofferbert.[6]
2. An ACE Trubore stirring shaft, bearing and Teflon stirrer blade turned on-end permit good stirring of the reacting solution.
3. Freshly distilled liquids must be used for best results. NMP (Aldrich or Eastman) is stored over Type 4A molecular sieves (Fisher Scientific) and distilled from CaH_2 under reduced pressure. Pyridine is stored over BaO and distilled from NaOH pellets. Triphenylphosphite is purified by vacuum distillation. Dried *p*-aminobenzoic acid from Aldrich (mp 188-189°C) is pure enough to be used as received. LiCl is dried at 180°C for 24 hours.
4. The inherent viscosity is measured at 25°C using a 0.1% solution in 96% H_2SO_4, with a Cannon-Ubbelohde viscometer having a solvent flow time of at least 150 seconds. The checkers obtained poly(*p*-benzamide) of inherent viscosity 1.3 dl/g.
5. Additional information about the lyotropic behavior of this polymer can be found in the literature.[11]

4. References

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