POLY(P-PHENYLENETEREPHTALAMIDE) OF HIGH MOLECULAR WEIGHT BY THE HIGASHI PHOSPHORYLATION REACTION

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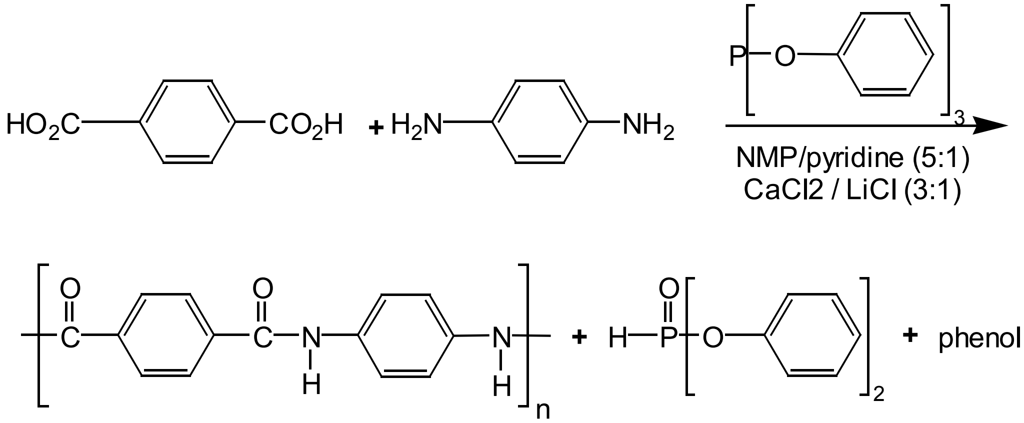

These reaction conditions were first reported by Higashi, Ogata and Aoki.[5]

1. Procedure

Into a constant temperature oil bath (Note 1) is placed a dry three-neck conical flask 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 nitrogen which is dried by passing it through a 20 cm column of Fisher 6-16 mesh S-160 silica gel. To the prepared vessel are added terephthalic acid (0.831 g, 0.005 mol) , *p*-phenylenediamine (0.541 g, 0.005 mol), a LiCl/$CaCl_2$ solution in pyridine/N-methyl-2-pyrrolidone (NMP) (Note 3) and triphenylphosphite (2.65 ml, 0.01 mol, Note 4). The oil bath is heated to 100°C and this reaction temperature is maintained for 3 h. The gel is removed using a spatula and ground in a blender jar containing methanol. The poly(*p*-phenyleneterephthalamide), PPD-T, is washed three times in the blender with 200 ml of methanol and refluxed with 200 ml of methanol for 1 h. After drying in a vacuum oven at 60°C to constant weight, the polymer yield is nearly quantitative. The inherent viscosity determined is 4.2 to 4.5 dl/g. PPD-T does not melt below 500°C.

2. Methods of Preparation

Poly(*p*-phenyleneterephthalamide) of high molecular weight can be prepared[6,7] by the reaction of terephthaloyl chloride with *p*-phenylenediamine in nonprotonic amide solvents, and this route is used commercially for the preparation of PPD-T.

PPD-T of somewhat higher molecular weight, 0_{inh} up to 6.2 dl/g, has been prepared[8] using conditions similar to those reported here.

3. Notes

1. The Techne TE-7/P oil bath is suitable for this experiment. It allows temperature control to within ± 0.5°C.
2. An ACE Trubore tubing shaft, bearing a Teflon stirrer blade turned on-end, is used to give good stirring of the reaction mixture.
3. To a dried Erlenmeyer flask having a ground glass stopper are added 50 ml NMP, 1 g LiCl, 3 g $CaCl_2$ and 10 ml of pyridine. This mixture is stirred with a magnetic stirring bar for 30 to 50 minutes to produce a slightly cloudy solution which is used in the polycondensation reaction.
4. For best results, the liquids used in the polycondensation reaction should be freshly distilled. NMP (Aldrich or Eastman) is stored over type 4A grade 513 molecular sieves (Fisher Scientific) and distilled from CaH_2 under reduced pressure. Pyridine is stored over BaO and distilled from NaOH pellets.

Purification of triphenylphosphite (Aldrich or Eastman) is performed by vacuum distillation. Terephthalic acid (Amoco) is of fiber grade purity and *p*-phenylenediamine is obtained from Fisher Scientific. LiCl and $CaCl_2$ can be dried at 180°C for 48 h.

5. The inherent viscosity was measured using a Cannon-Ubbelohde viscometer at 25°C using a 0.1% solution in 96% H_2SO_4.

4. Merits of the Preparation

The procedure given here is suitable for the preparation of all AA-BB aromatic polyamides, including those with all *para*-linkages, all *meta*-linkages, and mixed *meta*- and *para*-linkages.

5. References

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