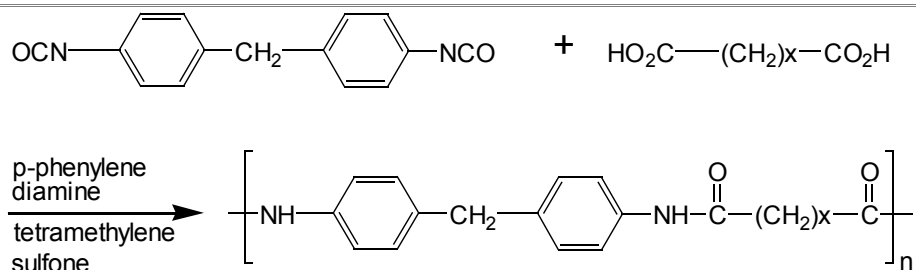


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This type of reaction was first described by Bayer<sup>3</sup> and the reaction conditions were modified by Onder and Grossman.<sup>4</sup>

## 1. Procedure

A dry 250 ml five-neck round bottom flask is placed in a constant temperature oil bath. The flask is fitted with a condenser, a mechanical stirrer (Note 1), an addition funnel, a thermometer 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 it through a 20 cm column of Fisher G-16 mesh silica gel. To this prepared vessel are added azelaic acid (13.16 g, 0.07 mol), adipic acid (4.38 g, 0.03 mol), benzoic acid (0.0452 g as a chain terminator), a catalytic amount of p-phenylene diamine (Note 2) and tetramethylene sulfone (TMSO, 100 g, 80 ml, Note 3). The mixture is stirred and heated to ca 220°C. A solution of 4,4'-diphenylmethane diisocyanate (MDI, 25.0 g, 0.1 mol, Note 4) in TMSO (25 g, 20 ml) is added dropwise over a period of 2 h (Note 5). The residual isocyanate in the addition funnel is rinsed into the reaction flask using more TMSO (10 g, 8.0 ml). After the addition is complete, the reaction mixture is stirred and maintained at the same temperature for 2 additional h. The prepared polymer is recovered by pouring the hot reaction mixture into 2 l of distilled water. The solid precipitate is then chopped by placing the water and precipitate into a stirrer-blender. The chopped strands are then continuously extracted with water using a Soxhlet extractor or by continuous washing with distilled water (Note 6). The solid polymer is then allowed to dry in air followed by 12 h at 90°C under vacuum. A polymer inherent viscosity of 1.0 dl/g is measured for a 0.5% solution in N,N-dimethylformamide (DMF, with 0.5 wt % LiCl, Note 7).

## 2. Methods of Preparation

Aromatic amine based polyamides of high molecular weight can also be prepared by the reaction of dicarboxylic acid chloride and a diamine,<sup>5,6,7</sup> or from the dicarboxylic acid directly using the Yamazaki<sup>8</sup> or Higashi phosphorylation reaction.<sup>9</sup>

## 3. Notes

1. An ACE Trubore stirring shaft, bearing and Teflon stirrer blade permit good stirring of the reaction solution.
2. Catalyst concentration is 0.25-1.00 wt-% of theoretical polymer yield (i.e., 0.084-0.337 g).
3. Freshly distilled tetramethylene sulfone with water content less than 500 ppm must be used which can be obtained by vacuum distillation over a suitable drying agent (LiAlH<sub>4</sub>).
4. High purity (99%) MDI, e.g. Isonate 125 M (Dow Chemical), should be used. Residual isocyanate dimer is removed by decanting off the pure MDI from a solution of monomer left overnight at 5°C.
5. MDI addition must be metered. Insoluble polymers were obtained when stoichiometric amounts of MDI and acids are combined in one portion.
6. Washing with water is done to remove residual TMSO. This can be checked by thermogravimetric analysis (TGA) which will show residual TMSO as a weight loss at 280-290°C. Residual solvent levels can be lowered to 1-3% by this method.
7. The inherent viscosity is measured at 27°C using an Ubbelohde viscometer (#75) by taking 0.25 g of the reaction mixture (which contains 20% solids) and dissolving it in 10 ml of DMF (with 0.5 wt % LiCl).

#### 4. Merits of the Preparation

The attractive features of this reaction include: 1) use of reactants which are tolerant of small deviations in stoichiometric equivalence; 2) easy removal of the volatile condensate, carbon dioxide; 3) high yields of polymer; and 4) generation of a wide range of aromatic polyamides.

#### 5. References

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