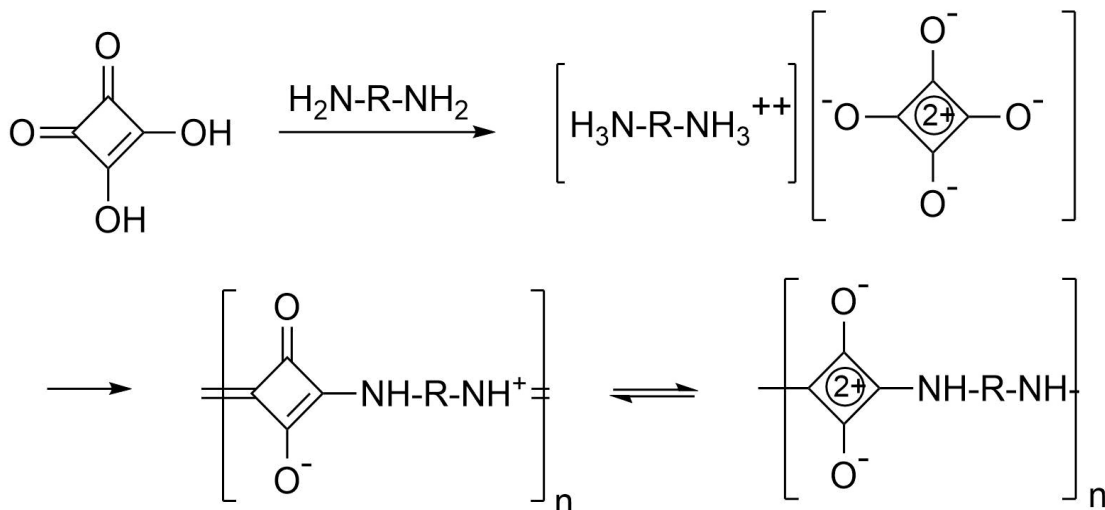


# Squaric Acid-1,3-Polyamides

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## 1. Procedure

### A. 1,6-Diaminohexane-Squaric Acid Salt

1,2-Dihydroxycyclobutenedione (squaric acid, 1.14 g, 0.01 mol) is dissolved in 15 ml of hot water. A solution of 1.16 g (0.01 mol) of 1,6-diaminohexane in 200 ml of acetone is then added, dropwise, with stirring. After cooling the squarate salt is removed by filtration and recrystallized twice from water-acetone, by dissolving the product in 5-10 ml of hot water and adding 150 ml of acetone in portions. There is obtained 2.1 g (90.8% yield) of salt (Note 1).

### B. Polyamide from Squaric Acid-1,6-Diaminohexane

#### Salt: Poly(azi-hexamer-alt-quadratyl-1,3-amer)

After 1 g of the salt is refluxed for 30 min. with 5 ml of *m*-cresol (Note 2), nearly all of the solvent is removed by distillation at atmospheric pressure for about 15 min. (About 4 ml). After cooling, the viscous liquid is stirred with 200 ml of acetone, and the polyamide crystallizes. The product is collected on a filter and recrystallized by dissolving in 2 ml of formic acid under reflux. After the volume has been reduced to 1 ml, the solution is placed in a refrigerator. A pale yellow polycondensate is obtained in 83-100% yield, mp above 350°. The polyamide shows low solubility in common nonpolar organic solvents (Notes 3 and 4). The viscosity ( $\eta$ )=0.06-0.163 dl/g in concentrated  $\text{H}_2\text{SO}_4$  as solvent at 20°.

### C. Polyamide from Squaric Acid and *p*-Phenylenediamine: Poly[azi-phenylene-(1,4)-azmer-alt-quadratyl-(1,3)-amer]

1,2-Dihydroxycyclobutenedione (squaric acid, 1.14 g, 0.01 mol) is refluxed with 1.08 g (0.01 mol) of *p*-phenylenediamine in 40 ml of glycerine for 10 min. About 10 ml of the glycerine is removed by distillation at atmospheric pressure for 15 min. to remove the water eliminate during the condensation. After cooling, the dark brown polycondensate is removed by filtration and extracted

with pyridine for 8 h. followed by extraction with methanol for 8 h. (Soxhlet apparatus) to yield 98-100% of product, mp above 350°. The viscosity of this aromatic polyamide could not be measured because of its very low solubility in concentrated sulfuric acid.

## 2. Characterization

The infrared spectra of squaric acid-1,3-polyamides resemble those of the monomer model compounds except that the bands are very diffuse and not as well resolved.

Carbonyl stretching frequencies appear at 1770-1841 and 1680-1730  $\text{cm}^{-1}$  <sup>3,4</sup> in the case of the squaric acid-1,2-bisamides, while the isomeric squaric acid-1,3-bisamides show no absorption in this region because of the quasi-aromatic character of the cyclobutene-diyliumdiolate system. [Ed. Note: Recent work has produced evidence that 1,2 as well as 1,3 orientations of the substituent links may be present in these systems.<sup>5</sup>]

Thermogravimetric measurements show that the polyamides with relatively long carbon chains between the cyclobutene-diyliumdiolate units are the most thermostable products of the squaric acid-polyamides which have been investigated. At a temperature of 350°, after heating for 2 h these polyamides lost 20-30% of their weight.

## 3. Notes

1. Preparation from the squarate salts is preferable to direct mixing of squaric acid and diamine because equimolar amounts of the components are essential for the attainment of high molecular weights. Also, purification of the components is easier by recrystallization of the squarates.
2. Because of their high boiling points and good solvent properties for both the squarates and the polycondensation products, the most suitable solvents for the preparation of the polyamides are cresols and glycerine. The condensation in cresol (with azeotropic distillation of water) yields nearly colorless polycondensates.
3. By dissolving the polyamides formed with 1,6-diaminohexane in formic acid and precipitating into dimethylformamide, in which the yellow, low molecular weight by-products are soluble, the purification can also be carried out with sulfuric acid and water.
4. From a formic acid, inorganic acid, or cresol solution transparent films can be formed. When heated in the presence of air, the polycondensation products darken when the temperature is higher than 250°.

## 4. Methods of Preparation

Condensation of 1,2-dihydroxycyclobutenedione (squaric acid) with primary and secondary monoamines leads to the mesomeric squaric acid-1,3-bisamides derived from 1,3-bisaminocyclobutene-diyliumdiolate, not the squaric acid-1,2-bisamides.<sup>6,7,8</sup> [Ed. Note: However, see ref.<sup>5</sup>] Analogously, the free squaric acid forms the polycondensates described in Procedures B and C (with bifunctional aliphatic or aromatic amines).<sup>7</sup> This procedure has been described in the literature.<sup>9</sup>

In an alternative polymerization, the squarate salt of 1,6-diaminohexane in formic acid is heated under nitrogen, and the solvent is slowly distilled to yield a nearly colorless precondensate. This can be further condensed under nitrogen and then a vacuum by raising the temperature. Polyamides so prepared are colorless to pale yellow.

## 5. References

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