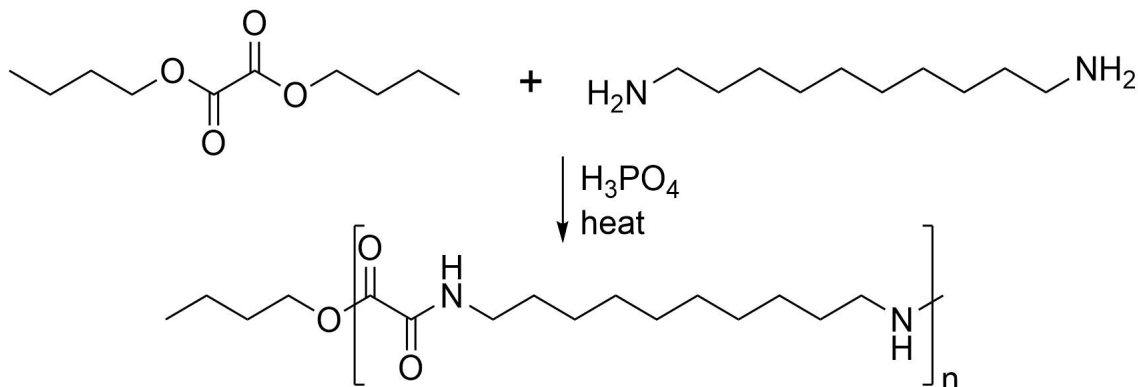


# Poly(decamethyleneoxamide)

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## 1. Procedure

Dry toluene (50 mL, Note 1), pure decamethylenediamine, (34.46 g, 0.20 mol, Note 2), and 1 mL of a 0.5% phosphorous acid in dry  $\text{CH}_3\text{OH}$  is prepared in a 300 mL, three-necked flask fitted with a  $\text{N}_2$  inlen tube, a stirrer, and a drying tube. The stirred, nitrogen-blanketed mixture is warmed to  $50^\circ\text{C}$  for complete dissolution, and pure di-*n*-butyl oxalate, (40.44 g, 0.20 mol, Note 3) is added quickly. The last few drops are washed in with a few mL of dry toluene. Heat is evolved (Note 4, a white solid precipitates, and the mixture soon becomes too thick to stir. The stirrer and drying tube are removed, the flask placed in a liquid metal bath and fitted with a distillation head and condenser. A 100 mL/min stream of dry  $\text{N}_2$  is introduced just above the surface of the prepolymer. The bath is brought to  $260^\circ\text{C}$  as rapidly as distillation of the toluene and butanol will allow. Heating is continued at that temperature for 2 h more (Note 5). The flask then cooled to room temperature under  $\text{N}_2$ . A tough, lightly colored, opaque, solid polymer is obtained on breaking the flask. It is soluble in a 7:10 by weight mixture of trichlorophenol and phenol;  $\eta_{\text{inh}}$  at  $25^\circ\text{C}$  for a 0.25% solution in trichlorophenol is 1.25 dL/g; the polymer melts sufficiently to be sticky at ca  $250^\circ\text{C}$ .

## 2. Notes

1. The toluene is dried over sodium.
2. Decamethylenediamine is available from Aldrich Chemical Co. It may also be made from sebacic acid according to directions found in the literature.<sup>3</sup> Be aware that diamines such as this absorb and react with carbon dioxide in the air to form carboxylate-ammonium salts. Because such salts give some substituted urea and water on heating, they consume diamine and limit molecular weight. Diamines should be stored in an atmosphere free from  $\text{CO}_2$ .
3. Di-*n*-butyl oxalate may be purchased from the Eastman Kodak Company or may be made by the method described for making diethyl oxalate in **Organic Syntheses**.<sup>4</sup> The diester is freed from half-ester by shaking or stirring in a blender with 10% by weight of finely divided dry calcium hydroxide. The ester is separated by filtration while protecting it from water. To test effectiveness, a 10 mL portion of the ester is added to 100 mL of distilled water containing a few drops of methyl orange in a glass-stoppered flask. It is immediately shaken vigorously for a few seconds. Reaction with the indicator indicates free acid and the treatment must be repeated. If not, the ester is fractionated through a 4 ft column packed

with glass helices and protected from contact with water in the atmosphere by drying tubes. The fraction boiling between 65.5°C/0.45 torr is suitable for polymer preparation.

4. If larger preparations are attempted, provision must be made for removal of heat by cooling the flask or by condensation of refluxing toluene and butanol in a condenser of appropriate size.
5. Heating at temperatures higher than 260°C results in lower molecular weight polymer, probably because of thermal degradation.

### 3. Methods of Preparation

Poly(decamethyleneoxamide) has been prepared by salt fusion<sup>5</sup> and polymerization in the solid state.<sup>6</sup> First use of oxalate esters is in an early patent of Carothers.<sup>7</sup> More recent patents on use of diamines and oxalate esters describe techniques similar to those used here.<sup>8,9</sup>

### 4. References

1. *Plastics Department, E. I. DuPont de Nemours and Co., Inc., Wilmington, DE 19898.*
2. *Monsanto Research Corp., Dayton Laboratory, Dayton, OH 45401.*
3. Horning, E. C. *Org. Syn. Coll. Vol.*, **1955**, 3, 229, 768.
4. Gilman, H. *Org. Syn. Coll. Vol.*, **1932**, 1, (1st Ed.), 56.
5. Carothers, W. H. U. S. Patent 2,130,948, September 20, 1938.
6. Flory, P. J. U. S. Patent 2,172,374, September 12, 1939.
7. Carothers, W. H. U. S. Patent 2,158,064, May 16, 1939.
8. Allen, S. J.; Drewitt, J. G. N. U. S. Patent 2,558,031, June 26, 1951.
9. Stamatoff, G. S. U. S. Patent 2,704,282, March 15, 1955.