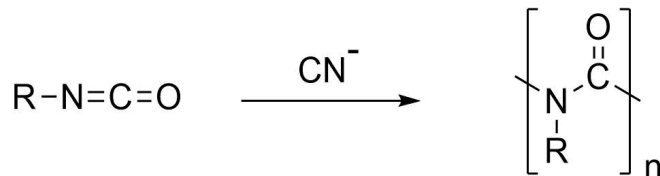


# Poly(N-hexyl 1-nylon)

Submitted by: V. E. Shashoua<sup>1</sup>

Checked by: R. W. Lenz and G. M. Scharlach<sup>2</sup>

---



## 1. Procedure

A 100 ml three-necked flask is equipped with a stirrer and two Y shaped side-arm adapters. One side-arm has a calcium chloride tube and a low temperature thermometer suitably placed for immersion in the reaction medium. The other side-arm is fitted with a nitrogen inlet tube, and the vertical arm is sealed with a rubber bulb. The flask is then flamed (Note 1) while being swept with nitrogen. This removes the traces of moisture adhering to the walls of the reaction vessel. Then 30 ml of dry N,N-dimethylformamide (DMF, Note 2) is added, and the flask and its contents are cooled to  $-58^\circ$ , approximately the melting point of DMF. Eight ml. of *n*-hexyl isocyanate is added to the reaction flask, and the mixture is stirred rapidly until the temperature reaches  $-58^\circ$  (Note 3). *Caution! Most isocyanates are potent lachrymators.* At this point, 4 ml of a solution of sodium cyanide in DMF (Note 4) is added dropwise during 2-3 min with a syringe, to the vigorously stirred reaction mixture. *Caution! Sodium cyanide is extremely toxic. Solutions in solvents such as DMF are rapidly absorbed through the skin.* The addition is carried out by piercing the rubber bulb at the side-arm with the syringe needle. The polymer precipitates immediately as a white solid. After stirring for 15 min at  $-58^\circ$ , 50 ml of methanol is added to quench the reaction. The polymer is then collected on a filter and washed with a total of about 300 ml of methanol. The product is then dried at  $40^\circ$  under vacuum to give 5.9-6.5 g of polymer (75-85% yield).

## 2. Characterization

*Solubility.* The polymer is soluble in most common aromatic and chlorinated hydrocarbons, such as benzene, chloroform, and methylene chloride. Films can be prepared by drying benzene solutions containing 2-5% polymer. The polymer degrades in concentrated sulfuric acid and trifluoroacetic acid.<sup>3,4</sup>

*Viscosity Measurements.* The inherent viscosity of the polymer should be 2.0-2.9 dl/g determined in benzene at  $30^\circ$  at a concentration of 0.1 g in 100 ml of solvent (Note 5).

*Melt Temperature.* The polymer melt temperature measured on a hot metal surface is  $195^\circ$ . The polymer softens at a temperature of  $120^\circ$ . This softening point is the temperature at which the polymer becomes plastic without sticking to the metal surface.

## 3. Notes

1. All flasks, pipets, and syringes should be thoroughly dried and flamed before use. The flaming of the moisture traces adhering to the walls of the glass equipment can be readily carried out

with a Bunsen burner. In the case of pipets, it is convenient to stopper the two ends with eye-dropper rubber bulbs to prevent reabsorption of moisture on their internal walls before letting them cool to room temperature.

2. The DMF must be dried before use by distillation from phosphoric anhydride at atmospheric pressure. Polymerization grade solvent can be prepared by starting with 2 l of DMF and 40 g of phosphoric anhydride. A fore-cut of about 600 ml is discarded and a middle fraction of about 800 ml of pure solvent is collected for use. To avoid a vigorous reaction of the P<sub>2</sub>O<sub>5</sub> with the DMF, which takes place in the pot residue, it is important not to allow the distillation to proceed to dryness.
3. The *n*-hexyl isocyanate can be synthesized by a method similar to that described by Boehmer.<sup>5</sup> Freshly distilled heptanoyl chloride (100 ml, Eastman Organic Chemicals) was added to 150 ml of toluene containing 46 g of activated sodium azide.<sup>6</sup> The mixture is heated under reflux until no further nitrogen is evolved. This generally takes about 4 h. The toluene solution is then decanted from the solid residue and distilled through a column packed with glass helices. The residue is fractionated twice, yielding 52 g of a clear white liquid, bp 162-163°.



It is found that this method of synthesis gives the best polymerization grade isocyanate. When the isocyanates were prepared from the amine hydrochloride and phosgene, extreme difficulty was experienced in obtaining polymerization grade product, probably because of the presence of traces of phosgene in the isocyanate.

4. The sodium cyanide catalyst solution is prepared by dissolving dry reagent grade compound in dry DMF to give a saturated solution containing 0.68%. The sodium cyanide may be dried over potassium hydroxide in a drying pistol for 2 days at 100° under vacuum.
5. The viscosity of the polymer and the molecular weight depend on the amount of catalyst used in the polymerization at a given temperature. Small amounts of catalyst give higher molecular weight polymers.<sup>4,7</sup>

#### 4. References

1. *Pioneering Research Division, Textile Fibers Department, E. I. DuPont de Nemours & Co., Wilmington, DE 19898.*
2. *The Dow Chemical Company, Framingham, MA 01701; current address Lenz - The University of Massachusetts, Amherst, MA 01002.*
3. Shashoua, V. E.; *J. Am. Chem. Soc.* **1959**, *81*, 3156.
4. Shashoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.
5. Boehmer, J. W. *Rec. Trav. Chim.* **1936**, *55*, 379.
6. Smith, P. A. S. *Org. Reactions* **1946**, *3*, 382.
7. Shashoua, V. E. U.S. patent 2,965,614, Dec. 20, 1960; *Chem. Abst.* **1961**, *55*, 10966c.