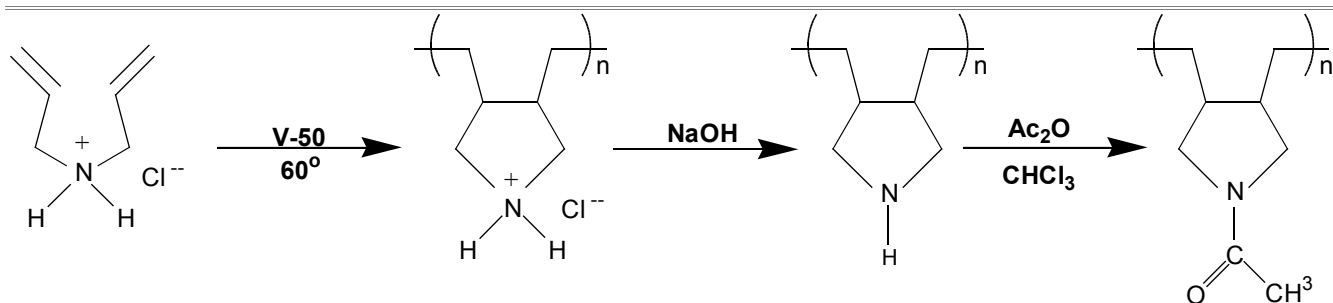


POLY(3,4-DIMETHYLENE-N-ACETILPYRROLIDINE)

Lon J. Mathias, Rajeev A. Vaidya and Terry B. Parsons¹

Checked by: George B. Butler and Jen-Chi Chen²



1. Procedure

a. Poly(3,4-dimethylenepyrrrolidine)

A portion of freshly distilled diallylamine (5.0 g, 0.0515 mol, Note 1) is dissolved in 6.18 g (10% excess) of concentrated hydrochloric acid (36% aqueous solution). The temperature is maintained close to 0°C throughout the dissolution process. The solution is degassed (Note 2) and transferred to a 30 ml jacketed reactor. Initiator (0.14g, 1 mol-% of V-50)³ is added to the stirred solution (Note 3). The reactor head-space is purged with nitrogen for 10 min. The nitrogen flow rate is then reduced to a minimum and fluid from a controlled temperature bath held at 60°C is circulated through the jacket (Note 4). Polymerization is continued with constant stirring under a nitrogen atmosphere for 24 h.

The highly viscous solution obtained is diluted with an equal portion of deionized water to reduce the viscosity to a manageable level. The diluted solution is cooled in an ice bath and twice the stoichiometric amount of 6N sodium hydroxide is slowly added to the stirring solution. The precipitated polymer (a tacky gel) is separated from the supernatant solution by filtration or decantation. The polymer is then washed with deionized water and lyophilized (Note 5). The polymerization has been carried out on small (5 ml) to large (250 ml) quantities of diallylamine with variable results. Conversions were usually in the range of 50-75%, although occasionally a polymerization did not go at all.

b. Poly(3,4-methylene-N-acetylpyrrolidine)

Finely divided poly(3,4-methylenepyrrrolidine) (2.0 g, 0.0206 mol) is dissolved in 30 ml of reagent grade chloroform. The polymer takes 4-5 h to dissolve and gives a cloudy solution that appears to be on the brink of phase separation. Acetic anhydride (6.31 g, 0.0618 mol) is added to the solution and the mixture allowed to react at room temperature for 24 h. The resulting polymer solution has a clear, light yellow color with no cloudiness. The polymer is precipitated by adding the reaction mixture to 300 ml of cold dry ether. The gelatinous precipitate is separated by decantation and washed with more dry ether. Finally, the polymer is dried under vacuum for 24 h to give 2.4 g of product (40% conversion, Note 6).

2. Characterization

The free polyamine is insoluble in most common organic solvents and forms cloudy solutions in chloroform. The structure is confirmed by IR and ¹³C spectra of solutions of the polymer in aqueous hydrochloric acid (Note 7, Spectra 1 and 2).

The acetylated polymer is very soluble in chloroform and gives an intrinsic viscosity of 0.5 dl/g (Note 8). The structure is confirmed by IR (thin film) and ¹³C (chloroform) spectra of the polymer (Note 9, Spectra 3 and 4).

3. Notes

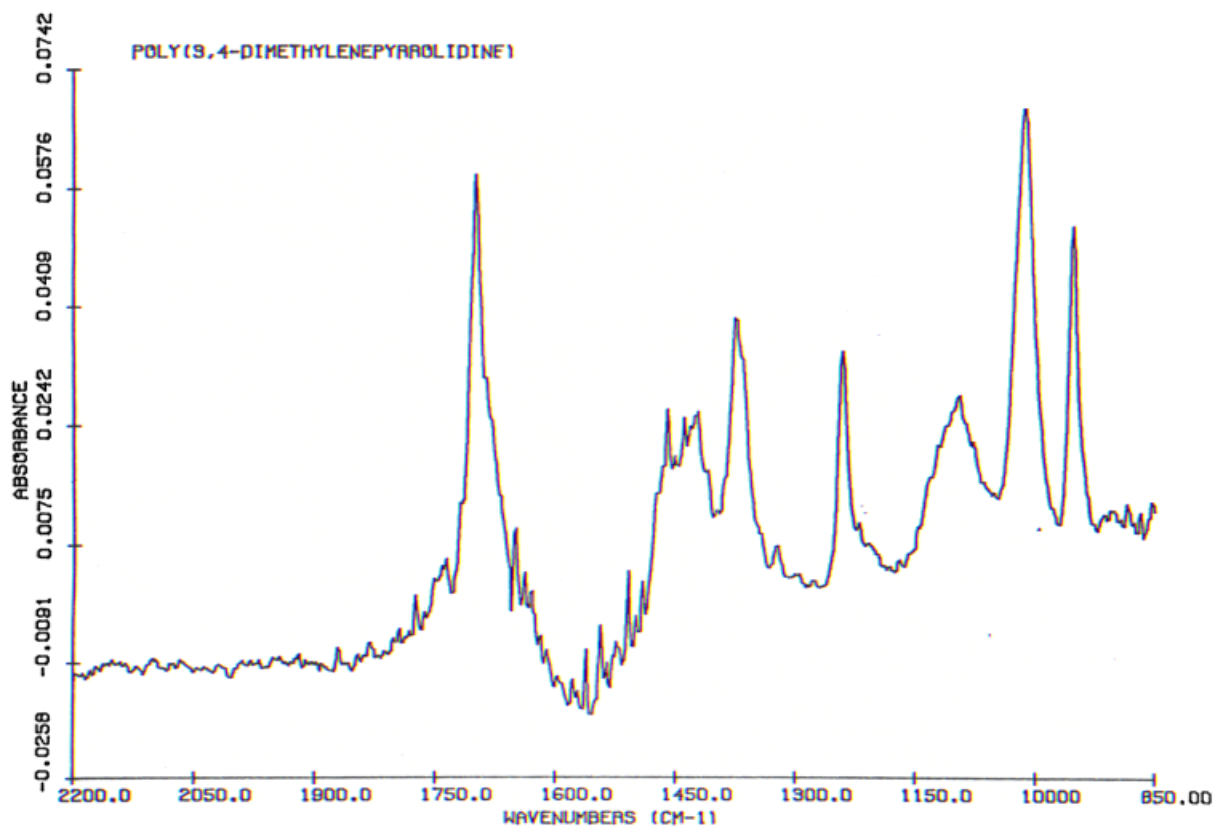
1. Commercial diallylamine (Aldrich Chemical Company) is 98% pure and is straw yellow in color. After vacuum distillation (60-65°C at 38 mm Hg), the monomer is colorless.
2. The flask containing the solution is evacuated while in the ice bath and the contents held under vacuum for 10 min.
3. *t*-Butylhydroperoxide (Lucidol, 90% aqueous solution) and a $\text{TiCl}_3/\text{H}_2\text{O}_2$ redox system⁴ have been used as initiators for the cyclopolymerization of diallylamine. However, V-50 gives cleaner, higher molecular weight polymer and faster rates of polymerization.³
4. A simple water or oil bath held at approximately 60°C may also be used.
5. Freeze drying is not necessary but gives an easily handled dry sample of polymer. Vacuum drying may also be used but usually results in the polymer collecting on the walls of the flask as a tough film. The checkers dialyzed their sample (Spectrum wet tubing with MW cut-off of 1000) and obtained a yield of 3.72 g (74% conversion).
6. Most of the acetic acid (by product of the acetylation) is removed from the polymer during the precipitation and washing steps. Acetic acid may be reduced to trace levels by repeating these steps. The checkers obtained 2.24 g (30% conversion) of acetylated polymer.
7. The IR spectrum is obtained in aqueous HCl using a Barnes Analytical Circle Cell³ and a Nicolet 5DX FTIR. The ¹³C NMR spectrum is obtained in aqueous HCl with a JEOL FX90Q (CH_3OH external reference).
8. Viscosities are measured at 30°C using a Cannon-Ubbelohde #50 viscometer. The checkers obtained an intrinsic viscosity of 0.32 dl/g.
9. The IR spectrum is obtained on a thin film cast from chloroform. The ¹³C NMR spectrum is obtained on a 30% chloroform solution.

4. Methods of Preparation

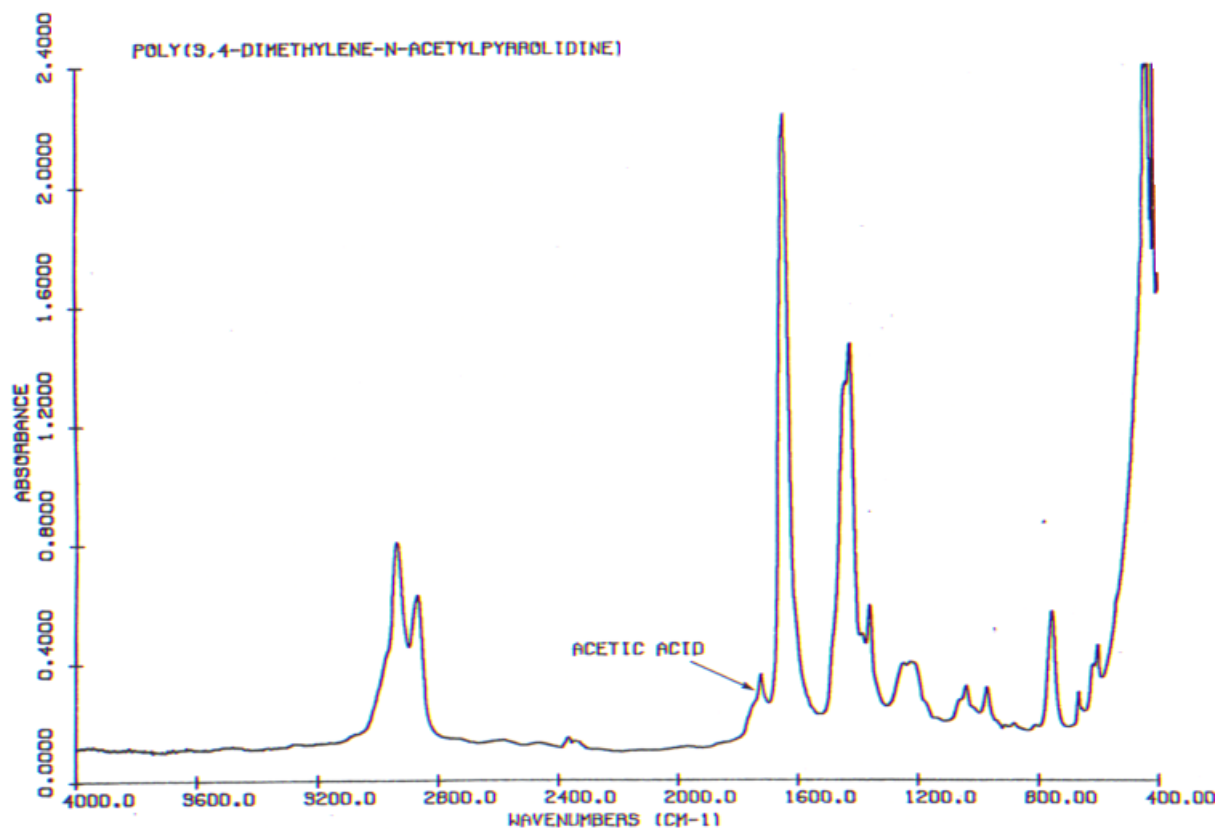
Diallylamine hydrochloride was one of the first monomers to be cyclopolymerized.^{6,7} The original polymerization was carried out using *t*-butylhydroperoxide, a very slow initiator, at 65°C for four days. The *N*-benzoyl derivative of the polyamine was prepared under Schotten-Baumann conditions.⁷ Copolymerization of diallylamine with diallylacetamide in aqueous HCl using ammonium persulfate as the initiator has been patented,⁸ but no information on yield or copolymer composition was reported.

5. References

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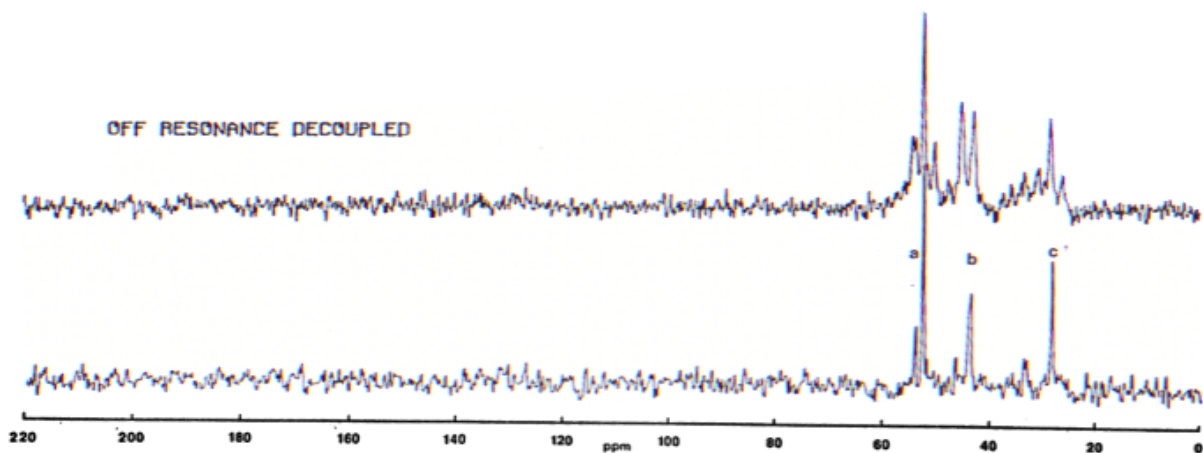
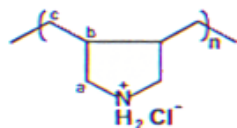


Spectrum 1. FT-IR of poly(3,4-methylene-pyrrolidine) in aqueous HCl.

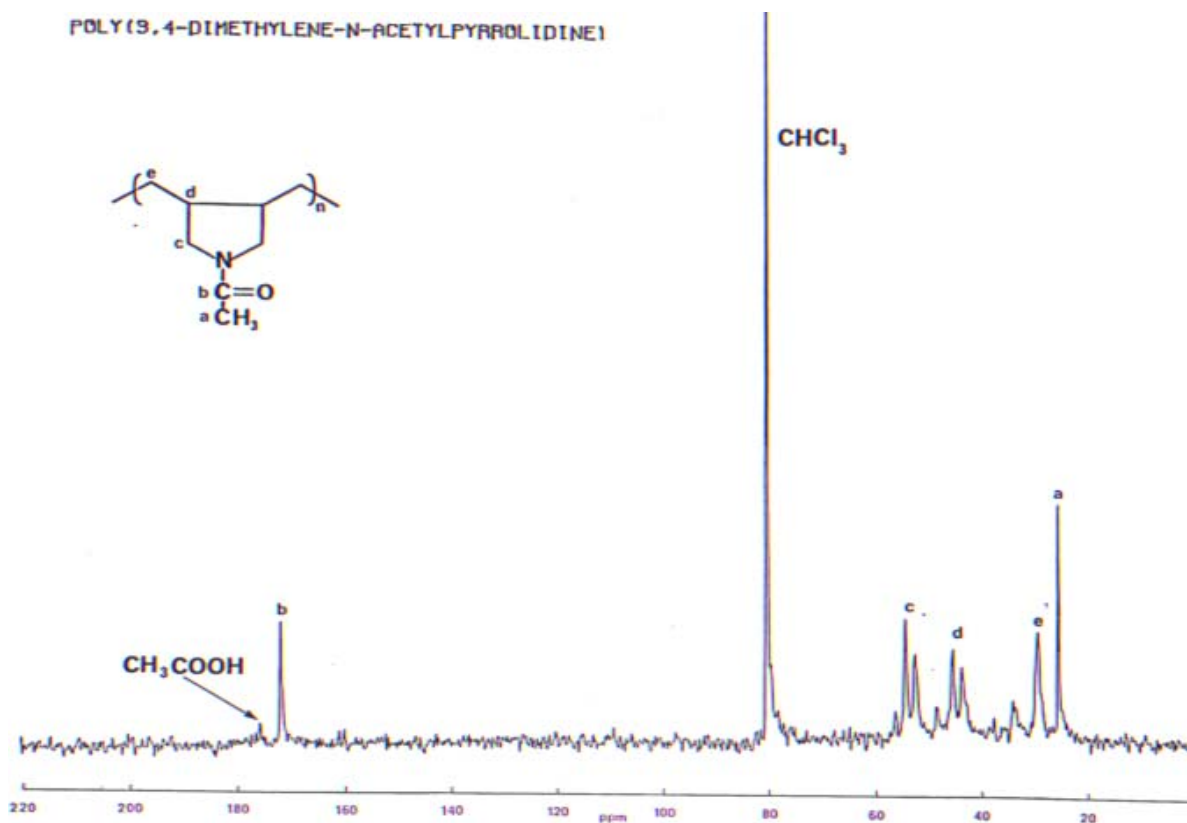
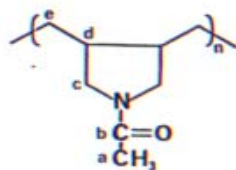


Spectrum 2. FT-IR of a thick film of poly(3,4-methylene-N-acetyl-pyrrolidine) cast from chlorine.

POLY(3,4-DIMETHYLENEPYRROLIDINE)

Spectrum 3. ^{13}C NMR of poly(3,4-methelenepyrrolidine) in aqueous HCl.

POLY(3,4-DIMETHYLENE-N-ACETILPYRROLIDINE)

Spectrum 4. ^{13}C NMR of poly(3,4-methylene-N-acetylpyrrolidine) in CHCl_3 .