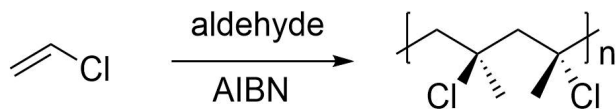


Crystalline Poly(vinyl chloride) Prepared in an Aldehyde Medium

Submitted by: I. Rosen ¹

Checked by: E. A. Ofstead and R. M. Pierson ²



1. Procedure

This method describes the preparation of a low molecular weight, highly crystalline poly(vinyl chloride) by a simple solution polymerization. Into a thick-walled polymerization tube (Note 1) of 200 ml capacity, which has been dried and flushed with prepurified nitrogen, is distilled purified vinyl chloride (62.5 g, 1.0 mol, Note 2). *Caution! Vinyl Chloride should be considered as toxic by inhalation and as a potential carcinogen. Distillation and subsequent venting should be conducted in a manner which avoids worker exposure.* While the nitrogen atmosphere is maintained, freshly distilled *n*-butyraldehyde (72 g, 1.0 mol) and 2,2'-azobis(isobutyronitrile) (AIBN, 16 g, 0.001 mol) are added (Note 3). The tube is sealed and transferred to a heating bath maintained at 50° (Note 4). The tube is agitated, or tumbled end over end in a bottle polymerizer, for 9 h (Note 5). The tube and its contents are cooled, the unpolymerized monomer carefully vented, and the contents poured, with stirring, into about 400 ml of methanol. The precipitated polymer is filtered (Note 6), then dissolved in about 80 ml of hot cyclohexanone (Note 7), and reprecipitated into methanol. After the polymer has been filtered and washed with methanol, the yield is about 9-15%. It is a white solid, difficultly soluble in tetrahydrofuran, and has a degree of polymerization of about 26. The polymer may be dissolved in hot cyclohexanone (120°). On cooling, the solution usually remains clear, and the viscosity can be determined.

The maximum melting point of 265° and the heat of fusion of 1180 ± 90 cal/mol have been determined by differential scanning calorimetry. The powder x-ray diffraction pattern shows a highly crystalline structure.³ Refined x-ray crystal structure analyses have been done. The infrared absorption spectrum is obtained from a film cast on a KBr disk from a chlorobenzene or *o*-dichlorobenzene solution. The high 635 cm⁻¹/692 cm⁻¹ infrared absorbance ratio relative to that of conventional poly(vinyl chloride) indicates increased syndiotacticity in the polymer (Note 8).^{4,5} NMR spectroscopy indicates racemic sequences (corresponding to syndiotactic placements) equivalent to those observed in PVC prepared at -65°.⁶ This method also works with other monomers (Note 9).

2. Notes

1. The polymerization may also be conveniently carried out in 8 oz "pop" bottles. A common 4 oz screw-cap bottle (able to withstand 100 psi) can be used with half the suggested quantities.
2. Vinyl chloride of adequate purity is obtained by distillation through an 18 in packed column. The first 10% of the distillate, as well as the last 10%, should be discarded. A good, polymerization grade vinyl chloride can be used directly without fractionation.
3. Increase of the mol ratio of aldehyde to vinyl chloride will decrease the yield of polymer without providing any significant increase in polymer crystallinity. The polymer crystallinity is so high as to be capable of little improvement.

4. Temperatures lower than 50° can be used with consequent reduction in reaction rate and little improvement in polymer crystallinity.
5. Increase of polymerization time will not significantly increase the polymer yield.
6. Some polymer is dissolved in the filtrate. This material may be recovered by evaporation of the solvent. It has a lower molecular weight than the precipitated polymer and is fairly crystalline.
7. The hot cyclohexanone solution may require filtration prior to the methanol precipitation step.
8. To characterize the structure, the infrared spectrum of the sample in the tacticity-sensitive 700-600 cm⁻¹ region was compared with those obtained from: (a) a "partly syndiotactic" sample prepared by free radical polymerization at -78°; (b) an "atactic" sample prepared by free radical polymerization at +50°; and (c) a "highly syndiotactic" sample prepared by the canal complex polymerization technique. The submitter's measurements of the 635 cm⁻¹/692 cm⁻¹ absorbance ratio placed the aldehyde-prepared sample between the values exhibited by (a) and (c). The checkers, however, found the spectrum to lie closer to (a). In any case, there is agreement that the procedure may be used for the preparation of at least a partly syndiotactic poly(vinyl chloride).
9. This method has been applied to the polymerization of vinyl trifluoroacetate and has provided a slight increase in polymer syndiotacticity.⁷

3. Methods of Preparation

Three other methods of preparing crystalline poly(vinyl chloride) have been reported in the literature: (a) the low temperature, free radical polymerization of vinyl chloride, in which advantage is taken of the energetically favored syndiotactic propagation over the isotactic propagation;⁸ (b) the polymerization of vinyl chloride in a urea complex, in which the monomer is supposedly oriented prior to polymerization and then polymerized by radiation⁹ (this polymerization takes place at -78° and raises the question of the relative amounts of the crystallinity caused by the low polymerization temperature and the complexing); and (c) the polymerization of vinyl chloride initiated by the Ziegler type of catalyst.¹⁰ [There is evidence that this polymerization is free-radical-initiated.¹¹]

4. References

1. *Diamond Alkali Company, Painesville, OH 44077; current address - Standard Oil Co., Cleveland, OH 44128.*
2. *Goodyear Tire and Rubber Co., Akron, OH 44309.*
3. Rosen, I; Burleigh, P. H.; Gillespie, J. F. *J. Polym. Sci.* **1961**, 54, 31.
4. Wilkes, C. E.; Folt, V. L.; Krimm, S. *Macromolecules*, **1974**, 6, 235.
5. Gouinlock, E. V. *J. Polym. Sci.* **1975**, A-2, 13, 1533.
6. Hassan, A. M. *J. Polym. Sci.* **1974**, A-2, 12, 655.
7. Matsuzawa, S.; Yamura, K.; Noguchi, H. *Makromol. Chem.* **1973**, 168, 27.
8. Fordham, J. W. L.; Burleigh, P. H.; Sturm, C. L. *J. Polym. Sci.* **1959**, 41, 73.
9. White, D. M. *J. Am. Chem. Soc.* **1960**, 82, 5678.
10. Hercules Powder Co., Australian patent 26,889, 1957.
11. Baker, W. P. *J. Polym. Sci.* **1960**, 42, 578.