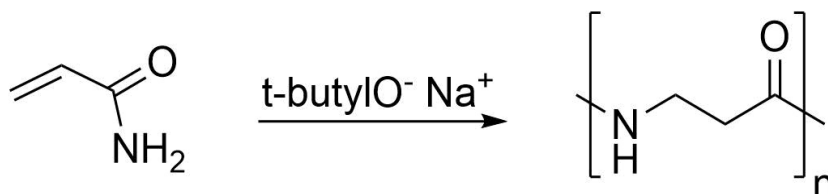


Polymerization of Acrylamide to Poly- β -alanine (Nylon 3)

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1. Procedure

In a 250 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, a reflux condenser carrying a drying tube, and a stopper are placed 0.02 g of *N*-phenyl- β -naphthylamine (Note 1) and 100 ml of dry pyridine (Note 2). Stirring is started, the mixture is heated to 95-100° on a steam bath, and 10.0 g of dry acrylamide (Note 3) are added. As soon as the acrylamide dissolves, a solution of 0.1 g of sodium in 10 ml of *t*-butyl alcohol (Note 4) is added. Polymer begins to form on the walls and stirrer in 3-10 min (Note 5). After 16 h of heating, the polymer is removed by filtration, extracted with 200 ml of water on the steam bath for an hour (Note 6), and dried overnight in a vacuum oven at 80° and 1 torr. The yield of water-insoluble polymer melting at about 335-340° (dec) is 2.8-4.8 g (28-48% of the theoretical amount). A 1% solution in 90% formic acid has a specific viscosity of 0.47-0.66 dl/g at 25° (Note 7).

After neutralization with acetic acid, the aqueous extract is evaporated to dryness to recover 3.2-3.6 g (32-36% of the theoretical amount) of water-soluble polymer melting at about 300-305° (dec) (Note 8). A 1% solution in 90% formic acid has a specific viscosity of 0.19 dl/g at 25°.

2. Notes

1. This is added as an inhibitor to vinyl polymerization. In small runs it may be unnecessary. This procedure has been used with up to 500 g of acrylamide.
2. Reagent grade pyridine allowed to stand over barium oxide for several days is suitable.
3. Commercial material may need to be sublimed at 0.1 torr before use. The checkers sublimed at 50° and 0.5-1.0 torr.
4. Because sodium dissolves slowly in boiling *t*-butyl alcohol, this solution must be prepared in advance.
5. If too much polymer forms on the stirrer, stirring can be discontinued without harm.
6. Because much of the polymer may adhere to the walls of the flask, it is convenient to carry out the extraction in the same flask.
7. The solution should be prepared just before the viscosity is determined. The strength of the acid used affects the viscosity considerably, stronger acids giving higher values.
8. During the evaporation some additional polymer may precipitate. After its removal by filtration or centrifugation, the evaporation is continued. If purification of the water-soluble polymer is desired, the evaporation should be stopped at a small volume and the solution poured into a large volume of methanol to precipitate 2.6 g of polymer.

3. Methods of Preparation

This method was discovered by Breslow, Hulse, and Matlack³ and studied further by Ogata.⁴ Low molecular weight poly- β -alanine has been prepared by the elimination of HX from a β -alanine derivative, $\text{NH}_2\text{CH}_2\text{COX}$ [where X is NH_2 ,⁵ OC_2H_5 ,⁶ Cl ,⁷ or OH ⁸]; by the elimination of thiophenol and carbon dioxide from N-carbothiophenyl- β -alanine;⁹ by base-catalyzed polymerization of 4,6-dihydro-1,3-oxazine-2,6-dione¹⁰ or the corresponding 1,3-thiazine;¹¹ and by polymerization of β -isothiocyanatopropionic acid. Molecular weights similar to those obtained by this procedure have been reported for the polymerization of perhydro-1,5-diazocine-2,6-dione.¹² Completely linear, high molecular weight poly- β -alanine has been prepared by polymerization of azetidine-2-one,¹³. Poly- β -alanine from acrylamide has been reported to contain some branching.¹⁴

4. References

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