Free-Radical Polymerization of 4-Vinyl Pyridine; N-Alkylation of the Polymer

{Poly[1-Butyl-4-Pyridinio)ethylene Bromide]}

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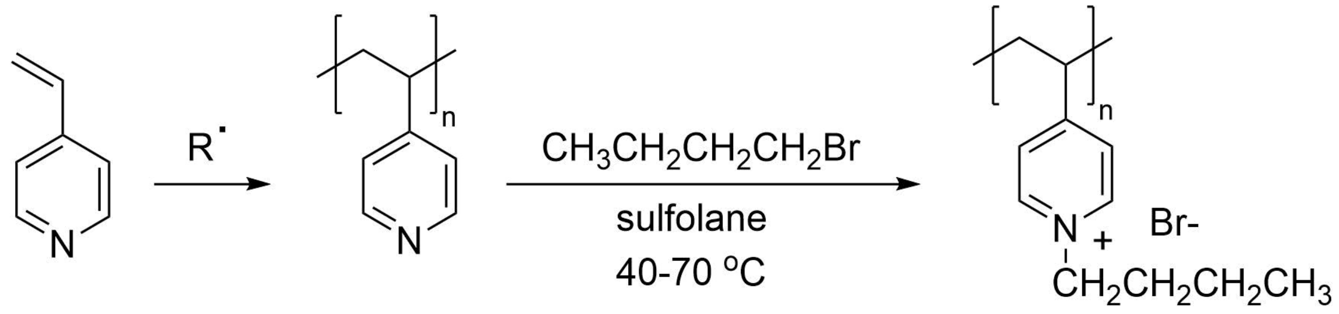

1. Procedure

a. Polymerization of 4-Vinylpyridine (4VP)

A solution containing 20 mL of freshly distilled 4VP (Note 1), 40 mL of methanol (Note 2), and 0.02 g of α,α'-azoisobutyronitrile (Note 3) is introduced into a polymerization tube which can be sealed. This vessel is connected to a high vacuum line (10^{-5} torr). The monomer solution is frozen and evacuated four times successively. The vessel is sealed to eliminate the influence of dissolved gas, especially oxygen, during the polymerization. After sealing, the polymerization vessel is maintained for at least 6 h at 60° in a thermostated bath. The solution becomes progressively viscous. At the end of the polymerization reaction a slight pink color may appear because of oxidation of the monomer, even under the careful conditions used.

The crude polymer is recovered by precipitation in ethyl ether. The polymer obtained is white. Further precipitations may be performed from methanol solutions, using dry ethyl ether as a nonsolvent. The polymer is dried under vacuum at 50°.

b. Alkylation of Poly(4-Vinylpyridine)

A convenient solvent for alkylation is tetramethylene sulfone (TMS; Note 4). A standard procedure is given for alkylation with butyl bromide (Note 5). P4VP (5 g) is added to 100 mL of TMS at 40° and the mixture is stirred until complete dissolution (Note 6). Butyl bromide (25g) is then added to the P4VP solution and the reaction vessel is maintained at 70° during the time of the reaction (Note 7). The reaction is carried out in a vessel equipped with a ground glass stopper, in the presence of air or under an oxygen-free nitrogen flow (Note 8). Magnetic stirring is maintained throughout the reaction.

The quaternized polymer is recovered by precipitation in dry ethyl ether. Because of its hygroscopic behavior the quaternized polymer must be stored in the absence of moisture.

2. Characterization

a. Poly(4-Vinylpyridine)

The molecular weight of poly(4-vinylpyridine; P4VP) is determined form measurement of its intrinsic viscosity in ethanol at 25°, using a viscosity/ molecular-weight relationship[3]:

$$[\eta] = 25.0 \text{ X } 10^{-5} M_w^{0.68}$$

b. Quaternized P4VP

During the alkylation reaction (or at its end) the percentage of alkylated groups can be determined by potentiometric titration of Br^- ions with 0.05 N $AgNO_3$ using a silver electrode and a glass reference electrode. An aliquot is taken and added to 25 mL of methanol and 2.5 mL of 2 N H_2SO_4 (to stabilize the glass electrode used as a reference). The addition of methanol stops the alkylation if the titration is carried out during the course of the alkylation reaction.

3. Notes

1. Purification of 4VP (a Fluka "purum" product). After washing with 0.1 N NaOH solution to remove the inhibitor and drying over calcium hydride, monomeric 4VP is distilled three times under reduced pressure in the presence of pulverized calcium hydride.
2. Methanol is a reagent grade product. Chloroform can be used alternatively as a solvent.
3. α,α'-Azoisobutyronitrile is Fluka "purum". Checkers recrystallized from absolute methanol.
4. Tetramethylene sulfone (Merck, mp 27°) is distilled under reduced pressure before use.
5. Butyl bromide is a Fluka "purissimum" product. It can be sued without further purification. However, if the bromide is slightly colored, distillation at 15 torr is required. Alkylation with other alkyl bromides such as hexyl or octyl bromide is quite similar.
6. The time needed for complete dissolution of the polymer can be as long as a few hours or more (depending on the molecular weight of the polymer).
7. When the percentage of pyridine groups quaternized is higher than 50%, the velocity of the reaction decreases strongly (the second-order velocity constant is reduced by one-tenth) and the time needed for complete alkylation increases dramatically.[3,4,5,6,7,8] At 70°, the alkylation with butyl bromide reaches a maximum after three days. If hexadecyl bromide is used, a week is necessary.
8. In the presence of air, at 70°, the solution in TMS becomes yellow because of colloidal sulfur originating from thermal decomposition and/or oxidation of TMS. This slight decomposition does not influence the properties of the alkylated polymer, which is white after precipitation.

4. References

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