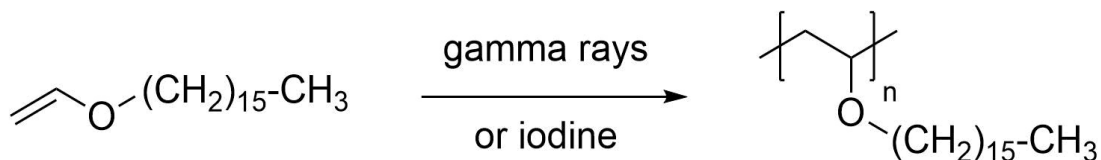


Poly(cetyl vinyl ether)

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1. Procedure

A. Radiation-Initiated Polymerization

Cetyl vinyl ether is polymerized at two temperatures. In each of two ampoules (Note 1) is placed 1 g of purified (Note 2) cetyl vinyl ether. Each sample is deoxygenated (Note 3) and sealed under 600 torr of nitrogen. The polymerizations are initiated by a Co^{60} radiation source (Note 4). During polymerization one ampoule is maintained at 12° and the other at 0° ; both samples are irradiated for 120 h. at a dose rate of 5.26×10^4 rad./h. The contents of each ampoule are dissolved in 5 ml of *n*-heptane at its irradiation temperature, and each polymer is then precipitated by adding each *n*-heptane solution to 500 ml of acetone stirred at -20° . The polymers are filtered on fine fritted glass filters and dried at room temperature in a vacuum chamber to constant weights to afford 0.63 g (63%) from the 12° polymerization and 0.38 g (38%) from the 0° polymerization.

B. Iodine-Initiated Polymerization

The inner surface of a 14 mm diameter glass ampoule is coated uniformly (to an approximate thickness of 0.02 mm) with 0.5 g of cetyl vinyl ether (Note 2). This is accomplished by melting the monomer at 40° , followed by rapid rotation of the tube at a 45° angle in an ice bath, so that an even, thin layer is obtained. The thickness of the layer is calculated from the surface area and the weight and density of the monomer. A separate glass vial containing 1 g of iodine is introduced into the polymerization ampoule at 0° , which is the polymerization temperature. The iodine is removed after 50 h. and the unreacted monomer is removed from the polymer by treating the reaction mixture with acetone at 0° . The product is filtered on a fritted glass filter and dried to a constant weight in a vacuum chamber to afford 0.26 g (52%) of poly(cetyl vinyl ether).

2. Characterization

Poly(cetyl vinyl ether) is soluble in *n*-heptane, benzene, petroleum ether, and tetrahydrofuran.

The viscosities of the polymers are measured with an Ubbelohde viscometer at 30° in tetrahydrofuran in the 0.1-0.4 g/dl range of concentration. The intrinsic viscosities of poly(cetyl vinyl ether) formed at 12° and 0° are 0.072 and 0.070 dl/g respectively; for the iodine-initiated polymerization at 0° the intrinsic viscosity is 0.078 dl/g (Note 5).

Procedures A and B both yield polymers with melting points of 39° . Until reaching the melting point, the polymers have a spherulitic structure. They exist as smectic double layers.

3. Notes

1. The ampoule is 200 mm long, has a 14 mm ID, and is equipped with a ground glass joint.
2. Before using the cetyl vinyl ether, it is advisable to distill it from metallic sodium at 115° (0.03 mm). The cetyl vinyl ether has a melting point of 16.5° and is in a smectic liquid crystalline state within the 16.5 to -2.5° temperature range. Further data concerning its crystalline structure are available.^{3,4}
3. The contents of the ampoule are frozen in ice. The ampoule is evacuated and blanketed with nitrogen, and the monomer is allowed to melt. This procedure is repeated three times before sealing.
4. A 500-Ci ⁶⁰Co source with panoramic construction has been used as an irradiation facility.
5. For numerical estimation of the DP values, the constants determined for poly(octadecyl vinyl ether) can be used.⁵ The reported intrinsic viscosities correspond to DP values of about 60-70.

4. Methods of Preparation

The iodine-initiated polymerization method has been adapted from the procedure used by Gy. Hardy, K. Nyitrai, and F. Cser.⁶

5. References

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