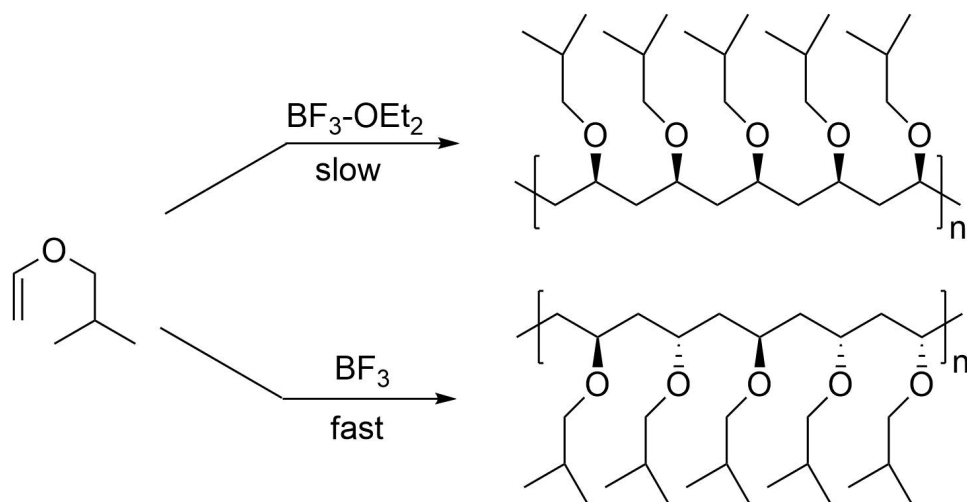


Stereopolymerization of Isobutyl Vinyl Ether

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A. Relatively Crystalline Isobutyl Vinyl Ether Polymers

1. Procedure (Proliferous Process)

Clean, granular Dry Ice (35 g) is placed in a 250 ml Erlenmeyer flask. The Dry Ice is in the form of granules of 1/8 to 1/4 inch size rather than a powder. To the Erlenmeyer flask is added 10 g of freshly distilled isobutyl vinyl ether (Notes 1 and 2). Liquid propane is condensed from a cylinder of Matheson C.P. propane into a 1 l Erlenmeyer flask surrounded by Dry Ice-acetone. To the cold 250 ml Erlenmeyer flask containing Dry Ice and isobutyl vinyl ether is added approximately 40 g of liquid propane. This reaction flask is cooled by immersing the lower half in a mixture of Dry Ice and petroleum ether in a Dewar flask. The flask may be plugged with cotton or glass wool.

In a 50 ml beaker, 0.20 ml of distilled boron trifluoride-diethyl ether complex is mixed from a micropipet with 5 g of granular Dry Ice. The Dry Ice containing absorbed boron fluoride etherate catalyst is transferred in portions during 10 min to the flask containing monomer, propane, and Dry Ice (Notes 3 and 4). In the reaction flask is placed a low temperature thermometer, and the fiber plug is again put in place. From time to time the flask may be removed from the Dewar flask for observation of the growth of polymer masses. The temperature of the reactants should not rise above -70° . If the liquid becomes viscous, or if the temperature rises with rapid evolution of carbon dioxide, the experiment must be repeated with purer materials and precautions to avoid local high temperatures and rapid reaction. If the polymerization is of the desired "proliferous" type,³ relatively hard, irregularly shaped polymer masses will have grown in the liquid medium during 1-2 h in the liquid medium which retains its low viscosity.

After 1-2 h of reaction the catalyst is deactivated or quenched by adding 10 ml of a mixture cooled below -70° and consisting of 4 parts by volume of methanol and 1 part by volume of 28% ammonium hydroxide containing 0.5% antioxidant (such as N-(p-hydroxyphenyl)morpholine or thymol). After thorough stirring, the flask is removed from the cold bath, the temperature is allowed to rise slowly, and the propane is allowed to evaporate. Precautions are taken against fire by working in an adequate fume hood. Sufficient methanol is added to cover the white polymeric

mass, and the mixture is allowed to stand overnight to facilitate removal of catalyst residues and to permit penetration of the polymer by the antioxidant. The polymer is washed twice with 100 ml portions of methanol and is dried to constant weight in a forced draft oven at 50°. Depending on the monomer purity, the temperature, and the mode of contact with the catalyst, isobutyl vinyl ether polymers of reduced viscosity (η_{sp}/C) 1.0-8.0 dl/g can be prepared (solutions of 0.10 g per 100 ml of benzene at 25°) (Notes 5 and 6) in yields of 80% - 100%.

Molded films of relatively crystalline isotactic isobutyl vinyl ether polymers are non-tacky, show cold-drawing, and have crystal melting ranges (by birefringence) of 90-120°. Molded films also show crystallinity by x-ray diffraction in both the drawn and the undrawn states. Quenching films by rapid cooling from above 100° to 0° results in lowered crystallinity as indicated by Shore A hardness. However, after 24 h, hardness and crystallinity are restored (Note 7).

B. Relatively Amorphous Isobutyl Vinyl Ethers Polymers

1. Procedure (Flash Polymerization)

Caution! These flash polymerizations in liquid propane diluent on addition of boron fluoride occur so rapidly with a burst of flammable gas that it is recommended that they be carried out only on a small scale in an efficient hood or, preferably, outdoors. Closed reactors are hazardous on a laboratory scale, but the open reactor may be covered with a screen to prevent ejection of the polymer by the violent reaction. A commercial process has been operated in Germany (Note 8).

In a 250 ml Pyrex® beaker cooled with Dry Ice-petroleum ether are placed purified isobutyl vinyl ether (10 g, Note 1) and 20 g of liquid propane. The beaker is removed from the cold bath, and the temperature of the monomer-propane mixture is allowed to rise to -60°. Into the middle of the liquid, gaseous boron trifluoride is passed from a 5 mm I.D. glass tube so rapidly that separate bubbles do not show distinctly. The boron trifluoride is not cooled before introduction. Almost at once, the polymerization occurs with a puff of gas that may throw some of the polymer into the air. The quenching, washing, and drying steps are the same as in procedure A, except that, because the soft product is not granular, it is cut into pieces about 1/4 in long before drying.

If the reaction requires long bubbling with boron trifluoride, or if the mixture only slowly becomes viscous, the procedure must be repeated with purer materials. Depending on the monomer purity, temperature, and exact mode of introducing the catalyst, rubbery amorphous polymers of reduced viscosity (η_{sp}/C) 0.5-5.0 dl/g can be prepared (0.10 g per 100 ml of benzene at 25°) (Note 9). Polymerizations with boron trifluoride gas that occur less violently, e.g., by a growth of polymer during 1 min, show more evidence of crystallinity but less than by procedure A. The amorphous polymers show halo-type x-ray patterns, Shore A hardness values from 0 to 5, pressure-sensitive adhesion, rubber-like extension with slow retraction, and films that cannot be cold drawn.

2. Notes

1. Commercial isobutyl vinyl ether monomer can be used as prepared from acetylene and isobutanol by the Reppe process (General Aniline and Film Corporation). Purer monomer may be obtained by washing commercial materials four times with an equal volume of water until substantially free of aldehyde (Tollens test). The monomer is dried by shaking it with pellets of potassium hydroxide and is allowed to stand overnight over fresh potassium hydroxide pellets. The monomer may be stored over solid potassium hydroxide or with a small amount of an amine as stabilizer against hydrolysis. For greatest monomer purity and polymers of highest molecular weight, the isobutyl vinyl ether may be refluxed for 1 h with metallic sodium wire before distillation. The monomer is distilled using a 2 ft Vigreux column; a fore-run of 10% and tail of 10% are discarded.
2. Closed agitated resin flasks may be used for polymerization, but evaporating Dry Ice inside the Erlenmeyer flask provides agitation. Some contact with moisture and air can be tolerated. Polymerizations of isobutyl vinyl ether without a solid phase of Dry Ice normally give less

isotactic polymer. However, boron trifluoride in solid benzene and certain other catalyst-solid solvent combinations give isotactic polymer without excess Dry Ice.

3. Instead of adding the etherate catalyst absorbed in a small amount of Dry Ice, the liquid etherate may be added directly if precautions are taken to prevent premature local reaction with rise in temperature. The cold droplets can be added in portions from a buret cooled to its tip by Dry Ice. If a homogeneous solution polymerization in propane begins, the viscosity and temperature will rise throughout and the reaction may run away in a few minutes.
4. The checker suggests that the addition of the catalyst adsorbed on Dry Ice can be made as fast as polymerization can be conducted without rise of temperature to higher than -70° . The checker obtained nearly quantitative yields in 20-30 min.
5. In these so-called prolific ionic polymerizations, values of η_{sp}/C rise during 10-15 min⁴. The polymerization seems homogeneous, although the system is actually heterogeneous.⁵
6. The checker obtained reduced viscosities of 3.47 and 3.04 dl/g for two "prolific" polymers obtained with method A.
7. The checker found little difference in crystallinity as measured by x-ray between films quenched in ice water after removal from the mold and those not quenched.
8. This flash type polymerization of isobutyl vinyl ether has been used in a continuous process by Badische Anilin und Sod Fabrik to make Oppanol C⁶.
9. The checker found reduced viscosity of 1.28 dl/g.

3. Methods of Preparation

Cationic polymerization conditions varying from those above have been observed to give poly(vinyl isobutyl ether)s of intermediate crystallinity. Thus, slower polymerization by diluted boron trifluoride gas gave moderate crystallinity,⁴ and prolific polymerization using boron trifluoride dissolved in methylene chloride as an immiscible catalyst gave crystalline polymers similar to those obtained using boron trifluoride-etherate.⁷ That the more crystallizable isobutyl vinyl ether polymers have the more regular meso structure was confirmed by Natta and co-workers.⁸ Lower monomer concentrations were found to favor formation of more isotactic poly(vinyl isobutyl ether),⁹ and polymerizations in homogeneous solution gave isotactic fractions of poly(vinyl isobutyl ether).¹⁰ Aluminum sulfate-sulfuric acid catalysts, which have been used commercially to prepare amorphous poly(vinyl ethyl ether),¹¹ were found to give partially isotactic poly(vinyl isobutyl ether).¹² The submitters found that isopropyl vinyl ether, which requires lower catalyst-to-monomer ratios than does isobutyl vinyl ether, gives substantially amorphous polymers by both procedures A and B.

Only the type A slow reaction gives high polymers from *n*-butyl vinyl ether. These are normally amorphous, but are substantially stereoregular because films and filaments crystallize on stretching. Normally, crystalline polymers have been prepared by prolific polymerization of 2,2,2-trifluoroethyl vinyl ether from CH_2Cl_2 solution using BF_3 -etherate as catalyst.¹³ Poly(vinyl ethyl ether) of moderate degrees of crystallinity was prepared by procedure A, except for the use of an excess of fine granular Dry Ice and a monomer of exceptionally high purity.¹⁴

Vinyl isobutyl ether has been polymerized to isotactic polymer at -78° using modified Ziegler-type catalysts obtained by reaction of titanium tetrachloride with an aluminum alkyl.¹⁵ Poly(vinyl isobutyl ether) of crystalline melting point 117° was obtained using $\text{AlCl}(\text{C}_2\text{H}_5)_2$ as a catalyst.¹⁶ Polymers of vinyl isobutyl ether and other vinyl ether monomers possessing higher degrees of tacticity than those discussed above have been obtained by use of complex catalysts without refrigeration.¹⁷ Reaction products of vanadium chlorides with aluminum alkyls,¹⁸ metal sulfates with aluminum alkyls or alkoxides,¹⁹ and aluminum alkoxides with sulfuric acid²⁰ have been used for slow stereoregular polymerizations of vinyl ethers at $0-30^{\circ}$. Additional syntheses and applications of alkyl vinyl ether polymers have been discussed.²¹

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