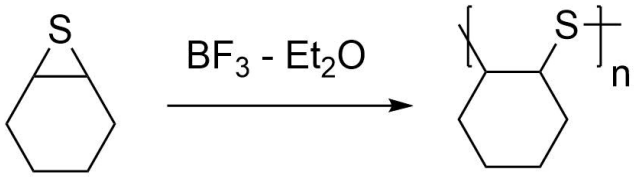
Poly(cyclohexene sulfide)

Submitted by: J. A. Empen and J. K. Stille [1]
Checked by: S. K. Das [2]



1. Procedure

In a nitrogen-filled glove bag (Note 1), a previously flamed 50 ml serum bottle is charged with (5 g, 0.044 mol, Note 2) of cyclohexene sulfide and 25 ml of anhydrous CH_2Cl_2 (Note 3). The bottle is capped and 0.28 ml (0.0022 mol) of BF_3 etherate (Note 4) is added through the septum with a calibrated syringe. The bottle is shaken occasionally during the addition and then allowed to stand at room temperature for 48 h.

The polymerization is terminated by the addition of 1 ml of CH_3OH, and the resulting polymer is isolated by evaporation of the solvent and drying under reduced pressure to give 4.5-5.0 g (90-100%) of poly(cyclohexene sulfide). The polymer is dissolved in 25 ml of $CHCl_3$ and reprecipitated into cold CH_3OH. After two reprecipitations, the polymer is lyophylized from benzene. The polymer prepared in this manner has an inherent viscosity of 0.2-0.3 dl/g (0.5 g/100 ml of chloroform at 25°). The poly(cyclohexene sulfide) has a glass transition temperature (T_g) of approximately -17°C and a softening point of 85-100°C (Note 5).

2. Notes

1. A collapsible glove bag from I^2R of Cheltenham, PA was used in these polymerizations.
2. Cyclohexene sulfide was prepared by the method of van Tamelen.[3] The monomer was heated under reflux over CaH and distilled from fresh CaH under nitrogen; bp 70°C/19 torr. It was necessary to distill monomer before each polymerization due to polymerization on standing.
3. Technical grade CH_2Cl_2 (Fisher Scientific Co.) was washed with conc H_2SO_4 until the acid layer remained colorless. The organic layer was washed with water, dried by refluxing over P_2O_5 and distilled from fresh P_2O_5. It was stored over 4A sieves (Linde).
4. Practical grade BF_3 etherate (Matheson, Coleman and Bell) was distilled under N_2 through a short Vigreux column before use; bp 126°C.
5. Transition temperatures were obtained on a DuPont model 900 DTA. Lower molecular weight samples may have a T_g as low as -50°C.

3. Methods of Preparation

Other catalysts have also proved successful for the polymerization of cyclohexene sulfide.[4,5] The bulk polymerization was too rapid and exothermic to allow sufficient control, however.

4. References

1. *University of Iowa, Iowa City, IA 52240.*
2. *Pittsburgh Plate Glass Company, Springdale, PA 15144; current address - PPG Industries, Allison Park, PA 15101.*
3. van Tamelen, E. E. *Org. Syn. Coll. Vol.* **1963**, *4*, 232.
4. Backsai, R. *J. Polym. Sci.* **1963**, *A(1)*, 2777.
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