**Polysulfide Liquid Polymer with Thiol Terminals**

Submitted by: E. R. Bertozzi

Checked by: P. H. Goble

1. Procedure

To a 3 L, three-necked, round-bottomed flask equipped with thermometer, 250 mL dropping funnel, reflux condenser, mechanical stirrer, and heating mantle, is added a solution of 1 L distilled water and 504 g Na₂S₉H₂O (2.63 mol, Note 1). Sulfur, 84.1 g (2.63 mol), is added with stirring. The temperature is raised to and held at 85-90°C until the sulfur is completely dissolved (about 30 min to 1 h) to form Na₂S₂₃. With sufficient stirring to obtain a moderately strong vortex, 10 g of 5% aqueous sodium alkyl aryl sulfonate, 16 g (0.2 mol) of 50% aqueous sodium hydroxide, and 81.3 g (0.1 mol) of 25% aqueous magnesium chloride hexahydrate are added.

Bis-2-chloroethylformal 346 g (2.0 mol, Note 3) is added to the dropping funnel. Bis-2-chloroethylformal is added gradually over a period of 90 min while the temperature is kept at 85-90°C. During most of the addition the mild exotherm may require some cooling. The deep orange-red color of the transparent sodium polysulfide solution gradually changes to an opaque, lighter orange-yellow color as polysulfide polymer is formed as 5-15 µm spheres. After all the bis-2-chloroethylformal is added, the temperature is raised to 95-100°C and held at this temperature with continued stirring for an additional 60 min.

Distilled water is added to the reaction mixture to fill the flask. Stirring is then stopped to let the polysulfide polymer dispersion settle to the bottom of the flask. The upper layer (excess sodium polysulfide) is siphoned carefully to minimize loss of polymer. This washing procedure is repeated once.

In a separate reactor 0.5 mol of Na₂S₂₅ is prepared by dissolving 120 g Na₂S₉H₂O and 20 g of sulfur in 500 mL of distilled water. This solution is added to the polysulfide polymer. The mixture is heated with stirring to 85-90°C and held at this temperature for 30 min.

Distilled water is added to the fill the reaction flask. The polymer is allowed to settle and the top, aqueous layer is siphoned. This washing cycle is repeated as many times as necessary to obtain an essentially colorless water layer. After the last cycle of washing and settling, the supernatant water layer is siphoned to leave a total volume of about 1.5 L (Note 4).

The temperature is raised to 85-90°C with stirring. Sodium sulfite, 94 g (0.765 mol) and 9.2 g of NaSH 2H₂O crystals (0.1 mol, Note 1) are added. The temperature is held at 85-90°C with stirring for 1 h (Note 5). The reactor is filled with water and the polymer is allowed to settle. The supernatant aqueous layer is siphoned.

The reactor is disconnected, and the dispersion of chemically reduced polysulfide polymer is poured into a 3 L beaker in a laboratory hood with good draft (Note 6). Glacial acetic acid is added to the polymer dispersion, which is hand stirred with a thick glass rod, to lower the pH from ca 10
to 4.5 - 5. Coagulation of the reduced polymer dispersion then occurs to produce an opaque cream-colored viscous mass. The aqueous layer is drained and the coagulum washed with 2 L of hot distilled water while mixed with a mechanical stirrer or hand-held spatula. The wash water layer is drained and washing is repeated at least four times.

The wet, clean coagulum is poured into a 1 L rotatable, round-bottomed vacuum drying flask heated with a 95-100° hot water bath. A vacuum source, such as a water aspirator, is used to produce a pressure of at least 25 mm. The polymer is dried to constant weight, at which point the polymer, light brown in color, is translucent or almost transparent. The yield is ca 250 g (75% of the theoretical amount). Viscosity should be between 15,000 and 80,000 cP at 25° (Note 7).

2. Notes

1. Na₂S and NaSH can be made by absorbing the corresponding equivalent of H₂S (free of mercaptan contamination) into NaOH in a good hood. It is not necessary to use the indicated sulfide hydrates.
2. The MgCl₂ forms colloidal Mg(OH)₂, which serves as the nucleating center for the polymer particles. Without it the particles would be widely dispersed in size and subject to premature mass coagulation.
3. Caution! Bis-2-chloroethyl formal is a toxic substance. It is made from ethylene chlorohydrin and formaldehyde. Preferably it should be a distilled fraction, free of acidity and free of monochloro compounds such as ethylene chlorohydrin that act as chain terminators.
4. At this point, the polymer has a molecular weight estimated to be in excess of 500,000. If a sample of the dispersion is filtered into a small cake and oven-dried, for example, at 75° for 24 h, an elastomeric solid results, having a Shore A hardness of ca 40.
5. At this point, a 5 mL sample of the mixture should be acidified with acetic acid to assess, qualitatively, the viscosity of the liquid polymer. If the polymer is more viscous than molasses or honey, an additional quantity of NaSH should be added and the mixture reacted for an additional 30 min.
6. Because some hydrogen sulfide is evolved, the acidification must be done in a hood.
7. The polymer should have a thio (SH) content of ca 0.8-2.5%. A sample of liquid polymer thoroughly mixed at room temperature with ca 10% by weight of lead dioxide powder should solidify to an elastomeric solid in ca 0.5-1.5 h, with a Shore A hardness of about 40 to 50. The lead dioxide causes oxidative coupling of terminal thiols to disulfide linkages, thus restoring the high molecular weight of the original polymer before reductive cleavage.

3. Methods of Preparation

The use of low mole fractions of trifunctional co-monomers such as 1,2,3-trichloropropane leads to branched polymers having higher moduli when the liquid polysulfide polymers are reoxidized to the high polymer. The use of higher levels of sodium hydrosulfide during the reductive cleavage step produces reduced polymers of lower viscosity (lower molecular weight) and therefore higher -SH content. [3, 4]

4. References

1. Thiolol Corporation, Chemical Division, Trenton, New Jersey 08607.