trans-1,4-Polybutadiene by Rodium Salt Catalysis in Emulsion

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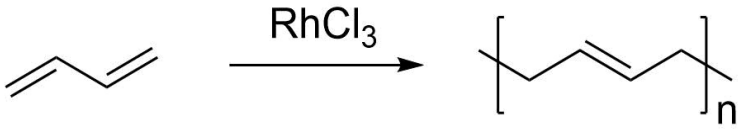

1. Procedure

In a 24 oz carbonated beverage bottle are placed 200 ml of distilled water, 5 g of sodium dodecylbenzene sulfonate (Note 1), and 0.5 g of "rhodium tichloride trihydrate" (Note 2). When this mixture has dissolved, the bottle is cooled in ice, then weighed on a balance in an efficient hood. Slightly more than 100 g of freshly distilled butadiene is carefully added. The excess butadiene is allowed to evaporate until the increase in weight is exactly 100 g. The bottle is quickly sealed (Note 3) with a metal cap provided with a small hole for venting, and fitted with a self-sealing rubber gasket and a nylon or Teflon® liner. The bottle and contents are warmed to room temperature before being placed on a rocker in a regulated bath at 50°. The emulsion begins to form almost immediately, and there is no induction period for the polymerization. The bottle is removed from the bath after 20 h (Note 4). Unreacted butadiene is vented (*Hood!*) through a syringe needle inserted through the hole in the cap. The cap is removed, and the emulsion is poured, with stirring, into 500 ml of methanol to which has been added about 0.5 g of N-phenyl-β-naphthyl-amine. The polymer is filtered, washed with more methanol, and dried under vacuum at room temperature; yd 25-30 g (Note 5). The polymer may be further purified by dissolving in 300 ml of chloroform, filtering or centrifuging, and reprecipitating into a stirred solution of 0.5 g of N-phenyl-β-naphthylamine in 500 ml of ethanol. The purified polymer is filtered and dried. The intrinsic viscosity of the product in chloroform at 30° is 0.4 dl/g. The *trans*-1,4 configuration represents more than 98% of the total unsaturation. The per cent crystallinity determined by x-ray diffraction is about 40%.

2. Notes

1. Suitable emulsifiers include alkali metal sulfonates and sulfates, such as sodium lauryl sulfate and sodium tetrahydronaphthalene sulfonate. Other anionic, cationic or non-ionic emulsifiers cannot be used.
2. Available from Engelhard Industries, Newark, NJ: 40% rhodium.
3. *Caution! The bottle should be protected with a metal screen or shield after sealing. The pressure from the butadiene can cause the bottle to explode as the contents warm to the temperature of the polymerization bath.*
4. A longer reaction time will lead to higher yields, but the emulsion becomes unstable. Considerable precipitate will be formed after about 20 h. This does not slow the polymerization nor does it affect polymer properties adversely.
5. Differences in the rate of polymerization may depend, in part, on the source of the rhodium chloride used. Rhodium salt from a different source gave 15-22 g of polymer.

3. Methods of Preparation

trans-Polybutadiene can be prepared by Ziegler-Natta catalysts.[3] Certain transition metal salts may be used in an emulsion recipe, rhodium being an outstanding example.[4,5]

4. References

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2. *The Goodyear Tire & Rubber Company, Akron, OH 44309.*
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4. Reinhart, R. E.; Smith, H. P.; Witt, H. S.; Romeyn, H. Jr. *J. Am. Chem. Soc.* **1961**, *83*, 4864; **1962**, *84*, 4145.
5. Canale, A. J.; Hewett, W. A.; Shryne, T. M.; Youngman, E. A. *Chem. & Ind. (London)* **1962**, 1054.