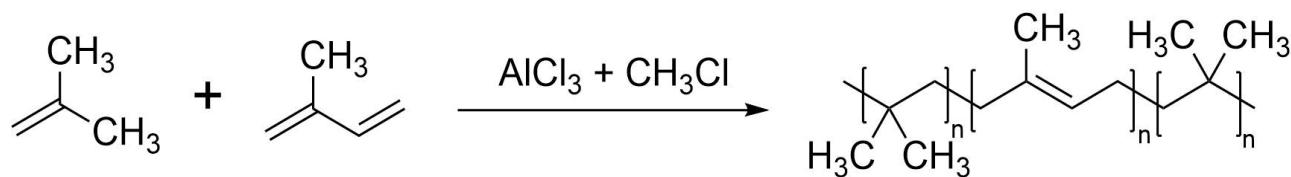


Butyl Rubber

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1. Procedure

Preferably in a dry box (Note 1) filled with nitrogen, a 1 l resin flask fitted with a thermocouple, stirrer, and two 250 ml jacketed addition funnels is immersed in a cooling bath maintained at -78°. To it is added 600 ml (at -78°) of methyl chloride (Notes 2 and 3). The two addition funnels contain (a) a mixture of 97 ml (-78°) of isobutene and 3 ml (-78°) of isoprene (Note 4), and (b) AlCl₃ in CH₃Cl solution prepared by refluxing 500 ml of CH₃Cl and 2-3 g of anhydrous, sublimed AlCl₃ for 3 h (Note 5), and filtering the obtained solution through a jacketed, medium-coarse fritted glass funnel (Notes 6-8). The contents of the dropping funnels are added dropwise to the vigorously stirred CH₃Cl (Note 9). Introduction rates: monomers 1-2 ml/min, catalyst 0.25-0.5 ml/min. After a short induction period, the polymerization starts (haziness). Temperature control is extremely important; the catalyst addition rate is reduced if temperature rises above -78°. After the introduction of the monomer feed, an excess of about 0.25 ml of catalyst is added and the slurry is stirred for 5 min more. The polymerization is terminated by adding 100 ml of pre-cooled methanol and stirring for 5 min. The unreacted gases are evaporated. The polymer is washed by kneading with methanol and dried under reduced pressure at 45-50° for 48 h; yd 75-85%; intrinsic viscosity 0.640-0.840, corresponding to 130,000-200,000 molecular weight (Note 10); mol % isoprene content 1.3-1.5 (Note 11); gel content less than 5%; second order transition point at ca -73°.

2. Notes

1. The checker found that satisfactory results can be obtained in the absence of a dry box with oven-dried glassware and connecting tubing, and by flaming the assembled apparatus while purging with dry N₂. All operations should be conducted in an efficient hood.
2. The methyl chloride gas is passed through two columns (1 m long, 3 cm radius filled with BaO) and condensed at -78° (Dry Ice and solvent). The jacketed addition funnels are cooled with a Dry Ice-pentane mixture.
3. The molecular weight of butyl rubber is strongly influenced by the reaction temperature. A plot of the logarithm of the molecular weight versus inverse temperature gives a straight line with a positive slope.³ Thus, higher molecular weight butyl rubber is obtained at T less than ca -100°C, the temperature of commercial operations. Convenient laboratory equipment for carrying out polymerization at extremely low temperatures (down to -190°) has been described.⁴
4. The isobutene is scrubbed with BaO (see Note 2 for methyl chloride); the isoprene is distilled.
5. Refluxing is at room temperature using a Dry Ice-pentane cold-finger reflux condenser.
6. The funnel is cooled with powdered Dry Ice in the jacket.

7. The concentration of the AlCl_3 catalyst solution should be 0.1-0.5 wt-%. For the analysis of AlCl_3 solutions, see ref 5.
8. Molecular weights are unaffected by catalyst concentrations in this catalyst concentration range.
9. *Caution! Operate safely! Because of the low flash points of isobutene and methyl chloride, particularly when working without a dry box, use sparkless motors, ground wires, exhaust hood, and Dry Ice and non-combustible solvent cooling baths.*
10. With a typical cationic polymerization system, butyl rubber molecular weights are extremely sensitive to reaction conditions (e.g., purity of chemicals, moisture, temperature fluctuations, and homogeneity of stirring among others) during synthesis. Using reasonably purified chemicals and care during polymerization, the specified molecular weight range should be attained. Molecular weights lower than about 130,000 are unacceptable when working at -78° and indicate inadequate care in preparation. Molecular weights are affected little by conversions within a wide conversion range (10-90%). The molecular weights are calculated from intrinsic viscosities obtained from single point measurements of 0.1% polymer solutions in di-isobutene at 20° by Flory's equation.⁵ The checker found that cyclohexane can be used if di-isobutene causes difficulties.
11. The isoprene content of butyl rubber is determined as mol percent unsaturation by the iodine-mercuric acetate method.⁶ A solution of butyl rubber in CCl_4 is reacted for 30 min with iodine in the presence of mercuric acetate and trichloroacetic acid, and the excess iodine is titrated with sodium thiosulfate. The iodine number (centigrams of iodine per gram of polymer) is multiplied by the factor 0.1472 to give mol-% unsaturation, and consequently, mol-% isoprene content.

3. Methods of Preparation

Preparation of butyl rubber by this method was first described in 1944.⁷ A convenient laboratory set-up has been described in detail.⁴

4. References

1. *Chemicals Research Division, Esso Research and Engineering Company, Linden, NJ 07036; current address, Institute of Polymer Science, University of Akron, Akron, OH 44309.*
2. *Thiokol Chemical Corporation, Trenton, NJ 08608.*
3. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953; p 218; Kennedy, J. P.; Squires, R. G. *Polymer* **1965**, 6, 579.
4. Kennedy, J. P.; Thomas, R. M. *Polymerization and Polycondensation Processes*; Advances in Chemistry Series 34, American Chemical Society: Washington, DC, 1962; Chapter 7.
5. Flory, P. J. *J. Am. Chem. Soc.* **1943**, 65, 372.
6. Gallo, S. G.; Wiese, H. K.; Nelson, J. F. *Ind. Eng. Chem.* **1948**, 40, 1277.
7. Thomas, R. M.; Sparks, W. J. U.S. Patent 2,356,128, 1944; U.S. Patent 2,356,130, 1944.