

Perdeuterio Synthetic-Natural Rubber

The recently reported stereospecific polymerization (1) of isoprene and the availability of D₂O has made possible the preparation of synthetic-natural (SN) rubber in which most of the hydrogen atoms are D atoms.

Acetone-d₆ was prepared (2) from 99.5 percent D₂O and acetone-h₆ in the presence of K₂CO₃. Nine stages were applied. Each required fractionation of acetone from water, and it is estimated that each replaced approximately half of the light hydrogen remaining from the previous stage. Acetylene-d₂ was prepared from D₂O and calcium carbide. The procedure of Bergmann (3) for the Favorskii (4) reaction of acetylene and acetone to form 2-methyl-3-buten-2-ol was followed except that in our work perdeuterio reactants were used.

The triple bond of the butynol selectively absorbed D₂ over the Lindlar (5) catalyst, and the resulting 2-methyl-3-buten-2-ol dehydrated readily over Al₂O₃ to give isoprene-d₈. Standard fractionation techniques were used for the isoprene and for all the intermediates. The isoprene was finally distilled over sodium to remove acetylenes, acetone, and alcohols. The same methods were applied to the corresponding perprotio derivatives. Table 1 gives the properties of most of the compounds prepared and used in this study.

The isoprene-d₈ polymerization was initiated by TiCl₄ and triisobutyl-h₂₇-aluminum in both aliphatic and aromatic solvents. Hydrogen from these solvents did not appear to interchange with deuterium from the monomer of polymer. Isoprene-d₈ polymerizes faster and to a higher molecular weight than isoprene-h₈ under what are believed to be comparable conditions. Our best sample of D-SN rubber was prepared by hexane extraction of a raw polymer containing 25 percent gel. The soluble polymer ($M_n = 333,000$) milled (broke down) like natural rubber and had a limiting intrinsic viscosity in benzene at 25° of $[\eta]_0 = 5.8$.

The benzene solutions were found to degrade unless they were stabilized with a small amount of tetramethylthiuram disulfide (TMTD). D rubber evolved (6) a trace of D₂ when it was vulcanized with TMTD and ZnO. The vulcanizate, after removal of zinc compounds and other substances by short-path distillation techniques (7), was nearly transparent and displayed an x-ray diffraction pattern that was superposable over those of natural and SN rubbers. The density at 23°C of the vulcanizate was 1.010 g/ml (equivalent to 1.009 at

Table 1. Properties of perprotio and perdeuterio derivatives of compounds and azeotropic mixtures.

Compound or azeotrope	Boiling point (740 mm)	Freezing point	Water (wt. %)	N_d^{20}	d_4^{20}
<i>Perprotio derivatives of compounds and mixtures</i>					
Acetone	55.3			1.3592	0.7895
Water	99.2	0.0	100	1.3333	0.99823
2-Methyl-3-buten-2-ol	103	3.0		1.4215	0.8609
2-Methyl-3-buten-2-ol water azeotrope	89.0	-10.5	27	1.4050	
2-Methyl-3-buten-2-ol	96.5	-28.0		1.4172	0.8231
2-Methyl-3-buten-2-ol water azeotrope	85.3	-9.0	23.2	1.4078	
Isoprene	33.3			1.4219	0.6802
<i>Perdeuterio derivatives of compounds and mixtures</i>					
Acetone	54.3			1.3565	0.8719
Water	100.6	3.8	100	1.3286	1.1075
2-Methyl-3-buten-2-ol	102	1.9		1.4188	0.9423
2-Methyl-3-buten-2-ol water azeotrope	89.5		27	1.4034	
2-Methyl-3-buten-2-ol	96.0	-28.8		1.4134	0.9185
2-Methyl-3-buten-2-ol water azeotrope	86.0		20.0	1.4053	
Isoprene	31.8			1.4189	0.7604

25°C); and the density of the polymer before cure was 1,005 g/ml (equivalent to 1.003 at 25°C). Accepting 0.906 g/ml at 25°C as the density of purified natural rubber (8) and multiplying this by the ratio (1.118) of the density of isoprene-d₈ to the density of isoprene-h₈ (see Table 1), we obtain a calculated value of 1.013 g/ml for the density of D rubber. Now the ratio of the formula weight (76.145) of isoprene-d₈ to that (68.119) of isoprene-h₈ is 1.118. It is probable that 0.906 is somewhat high as the density of perprotio all-*cis*, 1-4, head-to-tail polyisoprene, and values observed for some of our best samples of SN rubber are around 0.901. This, when multiplied by 1.118, gives 1.007 as the expected density of D-SN rubber. The good agreement between the found and expected values of the density shows that our specimen contains at most not more than a few hydrogen atoms.

Study of the boiling points given in Table 1 reveals, except for water where hydrogen-bonding is important, that the perdeuterio derivatives boil at lower temperatures than the corresponding perprotio compounds. Assuming boiling point to be a measure of molecular interaction in small molecules and to be of value for predicting segment interaction in a related polymer, it is expected that there would be less polymer-polymer interaction in the case of D rubber than in the case of H rubber. This expectation is confirmed by the interaction coefficient, μ_1 , found by study of toluene solutions which revealed a value of 0.415 compared with 0.398 for H-SN rubber. It is tempting to predict, therefore, that the dynamic properties of D rubber will be found to be better than those of H rubber.

The infrared spectrum of D-SN rub-

ber is of special interest. For example, it contains a band at 15.20 μ corresponding to the 11.95- μ band in H rubber. This finding confirms the previously somewhat doubtful assignment of the 11.95- μ wavelength to the H atom on the double bond.

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References and Notes

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Succinic Semialdehyde Oxidation by a Soluble Dehydrogenase from Brain

The identification of succinic semialdehyde as a product of transamination of γ -aminobutyrate by brain tissue (1) in vitro has led to an investigation of the further metabolism of succinic semialdehyde. Whole homogenates of rat, cat, and monkey brains have been shown to catalyze a diphosphopyridine nucleo-