Because of their questionable purity, the other liquid silazanes reported in this paper have been omitted.

The value of 2.00 ml. has been proposed by Warrick[12] for the silicon-nitrogen bond refraction. Application of Denbigh's[13] nitrogen-hydrogen bond refraction, 1.81 ml., to our silazane bond refraction indicates that the silicon-nitrogen bond refraction is 2.11 ml. It is possible that our value holds only for silazane bonds in compounds of the type from which it was derived.

Acknowledgment.—We are indebted to Mr. L. B. Bronk for the nitrogen analyses and to Mr. R. Northrup for some of the molecular weight determinations.

Summary

1. Alkyl-substituted cyclic and linear low polymers of the silazane series are described and compared with their siloxane analogs.

2. A refractometric constant for the silazane group has been derived.

SCHENECTADY, NEW YORK RECEIVED JULY 21, 1948

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[12] Warrick, THIS JOURNAL, 68, 2455 (1946).

[13] Denbigh, *Trans. Faraday Soc.*, 36, 936 (1940).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PHILLIPS PETROLEUM COMPANY]

Composition of Butadiene-Styrene Copolymers from Sodium-Catalyzed Polymerization

BY W. A. SCHULZE AND W. W. CROUCH

The composition of butadiene-styrene copolymers as a function of conversion in the GR-S emulsion polymerization system has been investigated thoroughly in connection with the synthetic rubber program. The styrene content of copolymer from this process is relatively low at the start of the reaction[1] (17.2% styrene in copolymer from a 75/25 butadiene-styrene charge) increasing at higher conversions as the butadiene is depleted from the system. This presumably indicates that the butadiene is the more reactive monomer in this peroxide-catalyzed emulsion reaction; however, due to the complexity of the emulsion system and the uncertainty of the concentrations of the monomers at the reaction loci, no definite conclusion can be drawn as to the rate constants of the reactions of each of the monomers with growing polymer chains.

In their study of the sodium-catalyzed copolymerization of butadiene and styrene, Marvel, Bailey and Inskeep[2] observed copolymers at all conversions to have styrene contents higher than that of the monomer charge, but no definite trend of composition with conversion was noted. Compositions of the copolymers were determined by means of ultraviolet absorption. In a further study of the sodium-catalyzed reaction, using catalyst preparation, polymerization and polymer recovery techniques somewhat different from those of Marvel and co-workers, we have employed refractive index measurements[3] to determine the composition of the copolymers with results showing styrene contents to be highest at low conversions and to decrease regularly as the reaction proceeds. Obviously, styrene is the more reactive monomer in this alkali metal-catalyzed reaction in contrast to the peroxide-catalyzed emulsion process in which the opposite has been shown to be the case.

It was of interest that the refractive indices of copolymers prepared by the sodium-catalyzed reaction are considerably lower than for polymers of the same composition prepared by the emulsion reaction. This was substantiated with samples of known compositions prepared by reacting to complete conversion charges of various proportions of butadiene and styrene. Results are presented graphically in Fig. 1 in which the refractive indices are shown as a function of styrene contents of polymers from both processes, the line for GR-S being from data of Madorsky and Wood.[4] From this correlation of refractive index with styrene

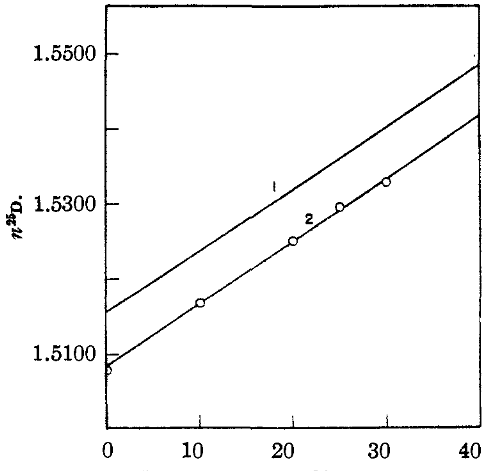

Fig. 1.—Refractive index of copolymers: 1, from emulsion reaction (data of ref. 4); 2, sodium-catalyzed reaction.

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[1] Meehan, *J. Polymer Sci.*, 1, 318 (1946).

[2] Marvel, Bailey and Inskeep, *ibid.*, 1, 275 (1946).

[3] W. O. Baker and J. H. Heiss, Jr., private communication.

[4] Irving Madorsky and L. A. Wood, National Bureau of Standards, private communication.

content, compositions were determined of polymers taken at various conversions from the sodium-catalyzed reaction. Results are shown as the points of Fig. 2.

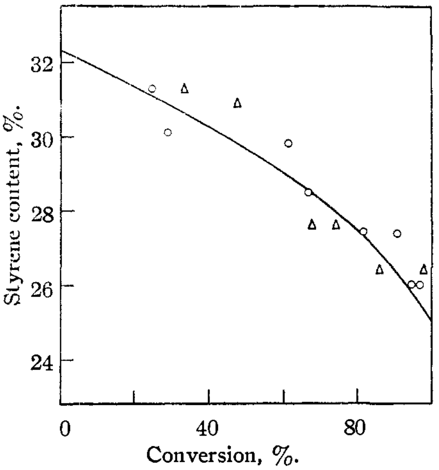

Fig. 2.—Styrene content of sodium-catalyzed copolymers: ○, 40° with isobutane diluent; △, 30° without diluent.

Under certain conditions[5] reaction rate constants throughout the reaction of two polymerizing monomers may be related[6] by the equation

$$\frac{dn_x}{dn_y} = \alpha \frac{n_x}{n_y}$$

in which n_x and n_y represent the number of molecules present of monomers x and y and α is the ratio of their reaction rates with growing polymer chains. From additional equations derived by Meehan[1] the composition curve of Fig. 2 was calculated for a 75/25 butadiene–styrene charge, assigning to α a value of 0.70.

One established difference between peroxide and sodium-catalyzed butadiene polymers is the higher vinyl side-chain content of the latter.[7] It is to this difference in structure within the polymer chains that the difference in refractive indices of the two types of polymers is attributed. As further evidence that this is the case, butadiene was polymerized at various temperatures with sodium catalysts to provide polymers of varying vinyl side-chain contents.[7] Results were

Polymerization temperature, °C.	External double bonds, %	n^{25}_D
20	58	1.5080
40	54.5	1.5090
60	47.5	1.5110

The increase in refractive index with decrease in external double bonds is in the direction to account for the difference observed between products of sodium-catalyzed mass polymerizations and emulsion reactions. It is recognized, however, that other differences in structure may be involved; for example, as a result of internal cyclization[3] of the sodium-catalyzed polymers or from differences in the end groups of polymer chains.

Experimental

Purification of Monomers.—Phillips Petroleum Company Special Purity 1,3-butadiene was drawn from storage liquid phase, vaporized, passed gas phase over calcium chloride desiccant and condensed in a steel cylinder prior to charging to polymerization reactors. Pure Grade isobutane was treated in the same way and blended with an equal weight of butadiene for use in those reactions requiring a diluent. Dow and Company 99.5% styrene was purified by fractionation in a Vigreux column, discarding the first 10% overhead.

Preparation of Catalyst.—Merck and Company Reagent Grade sodium metal was dispersed in dry xylene by a modification of the procedure of Morton and co-workers[8] using a high speed agitator in a creased glass flask at 110°. Nearly all the catalyst particles had diameters in the range of 10 to 50 microns. The dispersions were stored in cork-stoppered bottles and aliquots withdrawn in graduated pipets as required for polymerization charges.

Polymerization Procedure.—Aliquots of the catalyst dispersion were charged to 6-ounce glass beverage bottles after which the latter were cooled and placed on a balance and a cold stream of liquid butadiene or butadiene-isobutane mixture introduced at atmospheric pressure. While this step was in progress, styrene was charged from a pipet. When the required weight of butadiene had been received, the bottles were capped and agitated by rocking in a constant temperature water-bath. At the end of the polymerization period they were vented to remove isobutane and unreacted butadiene and broken to recover the polymers. These were transferred to a wash mill where the catalyst was removed and phenyl-β-naphthylamine antioxidant added. Finally, the products were dried for twenty-four hours in a mechanical convection oven at 65°.

Styrene contents were determined as a function of conversion with two different recipes and reaction conditions:

	Recipe no. 1	Recipe no. 2
Butadiene	75 parts	75 parts
Styrene	25 parts	25 parts
Isobutane	75 parts	0 part
Sodium	0.40 part	0.30 part
Reaction temperature	40°	30°

Copolymers of known styrene contents were prepared by use of Recipe no. 2 varying the proportions of butadiene and styrene to give the required compositions. These were polymerized for periods of fifty hours or longer to assure complete conversion. Polymerization times for copolymers of varying conversion were in the range of four to twenty hours.

Determination of Refractive Indices.[4,9]—The dried copolymers were passed three times through a laboratory mill set at 0.030 inch and the resulting sheets cut into strips 1 mm. wide and 5 mm. long. One-half gram samples were extracted at 80° for two hours with each of two 50-ml. portions of a 30 volume per cent. solution of toluene in absolute ethanol (ethanol–toluene azeotrope). The extracted strips were washed with three portions of fresh ethanol–toluene mixture and finally with acetone, then dried for three hours in a vacuum oven at 100°. They were then milled into sheets of 0.003 to 0.005 inch thickness which were cut to the proper size and placed on the prisms of an Abbé refractometer for the refractive index determinations.

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(5) Assuming that the relative reactivities of the monomers with growing polymer chains are the same with chains having previously reacted with either of the two monomers.

(6) Wall, This Journal, **63**, 1862 (1941).

(7) Kolthoff, Lee and Mairs, *J. Polymer Sci.*, **2**, 220 (1947).

(8) Morton, Davidson and Newey, This Journal, **64**, 2240 (1942).

(9) The authors gratefully acknowledge the assistance of J. E. Burleigh who performed the refractive index determinations and of C. A. Uraneck for determinations of external double bonds.

External Double Bonds.[9]—This determination was made by the reaction with perbenzoic acid by a modification of the method of Kolthoff and Lee.[10]

Summary

By means of refractive index measurements, styrene contents have been determined as a function of conversion of products from the sodium-catalyzed copolymerization of butadiene with styrene. Results show styrene to be the more reactive monomer, in contrast to the reaction in emulsion systems.

Refractive indices of sodium-polymerized products are lower than of copolymers from emulsion reactions. This difference is postulated to be due to higher proportions of external double bonds in the former.

[10] Kolthoff and Lee, *J. Polymer Sci.*, **2**, 206 (1947).

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

The Electrophoretic Mobility of Type III GR-S Latex

BY S. H. MARON AND W. W. BOWLER[1]

Introduction

Type III GR-S latex is a negatively charged colloidal dispersion of butadiene-styrene copolymer particles in an aqueous medium. The latex is prepared by emulsion polymerization of equal weights of the monomers in the presence of the potassium soap of K-wood rosin as emulsifier. As it appears on the market the latex is stripped of unreacted monomers, and contains neither a shortstopping agent nor an antioxidant.

In a preceding paper from this Laboratory[2] were reported the effects of various factors upon the electrophoretic mobility of Type II GR-S latex. Type II latex differs from Type III in being stabilized by fatty acid soap rather than rosin soap, and in being prepared from a 3:1 proportion by weight of charged butadiene–styrene rather than 1:1. It is of interest, therefore, to determine how these altered conditions influence the mobility, and, in turn, the stability, of Type III latex. Consequently, effects of total solids content, *p*H, ionic strength of added electrolyte, temperature, and soap content on the mobility of Type III latex have been investigated and are reported in this paper. Also given here are the zeta potentials calculated from the data.

Experimental

The moving boundary apparatus and procedure employed were essentially the same as described previously.[2] Disodium phosphate solutions containing a trace of potassium chloride were used as the electrolyte added to the latex, and for the leading and following solutions. For a latex solution 0.05 molar in disodium phosphate, and having a specific conductance of 0.0082 ohm^{-1}, the optimum current through the cell was found to be 1.5 milliamperes. Currents greater than 1.5 milliamperes tended to produce diffuse boundaries and to give uncertain mobility values. For other solutions the current was varied as the square root of the specific conductance on the basis of 1.5 milliamperes for the above 0.05 molar disodium phosphate solution.

Mobilities were calculated from the migration rates of both the advancing (descending) and receding (rising) boundaries, and the averages taken. The mobilities from the two boundaries agreed generally within ±1.5%, and were apart *ca.* ±5.0% only in solutions of low *p*H where the latex solutions were highly unstable.

Three different cells were used in the present work, two constructed from *ca.* 8 mm. and one from 7 mm. Pyrex tubing. All cells gave the same results for a given sample.

Except when otherwise noted, the temperature for all experiments was 30.00 ± 0.05° and the *p*H between 8.7 and 9.3. In experiments where the *p*H was varied, the ionic strength was maintained constant by addition of appropriate quantities of hydrochloric acid or sodium hydroxide to the disodium phosphate buffers. In the runs with added soap, the soap was added to the latex and the solutions adjusted to a disodium phosphate ionic strength of 0.05. No cognizance was taken of the contribution made to the ionic strength by the added soap.

All conductivity measurements were made with a Leeds and Northrup Campbell-Shackelton bridge assembly and Jones Type B conductivity cell. The viscosities of the latex solutions were determined with an Ostwald–Cannon–Fenske pipet, while the densities with Weld Type pycnometers. A Beckman Type G glass electrode assembly was used for all *p*H measurements.

The Type III latex used in this work was a commercial product of originally *ca.* 40% solids. This latex was diluted with distilled water to give a stock solution of 21.7% total solids, 0.0378 normal soap and 0.0037 normal free rosin acid content. All solutions upon which measurements were made were prepared from this stock solution by further dilution with distilled water.

Effect of Various Variables on Electrophoretic Mobility

(1) **Total Solids Content.**—It was found possible to get sharp boundaries and concordant mobilities from both advancing and receding boundaries only with latex dispersions of 7–15 g. per liter of total solids. Below 7 g. per liter streaming of the latex produced diffuse boundaries. Above 15 g. per liter the receding boundary became diffuse and yielded a progressively smaller mobility as the concentration increased, while the advancing boundary remained sharp and gave the same mobility as in the more dilute range. In view of this behavior all runs were made at a concentration of 12 g. of latex solids per liter where both boundaries migrated with the same velocity.

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[1] The Firestone Tire and Rubber Company Research Fellow, 1946–1948. Present address: The Firestone Tire and Rubber Company, Akron, Ohio.

[2] S. H. Maron, D. Turnbull and M. E. Elder, THIS JOURNAL, **70**, 582 (1948).