A similar disproportionation is thought to have taken place in the present reaction, but further study is necessary before a definite statement of the reaction mechanism can be given. The fact that acetic acid was obtained as a product of the reaction, however, led to the assignment of the structure $\mathrm{CH_3CCl_2OCF_2CFHCl}$ to the compound.

(G) $\mathrm{ClCH_2CH_2OCF_2CFHCl}$.—The structure of this compound was determined by synthesis according to the equations

$$\mathrm{HOCH_2CH_2OH} + \mathrm{CF_2{=}CFCl} \xrightarrow{\mathrm{HOCH_2CH_2O^-}} \mathrm{HOCH_2CH_2OCF_2CFHCl}$$

$$\mathrm{HOCH_2CH_2OCF_2CFHCl} + \mathrm{PCl_5} \longrightarrow \mathrm{ClCH_2CH_2OCF_2CFHCl} + \mathrm{HCl} + \mathrm{POCl_3}$$

Ethylene glycol was added to trifluoroethylene under autogenous pressure[17] in the presence of sodium 2-hydroxyethoxide in a Parr hydrogenation apparatus. The resulting 1-(2-hydroxyethoxy)-1,1,2-trifluoro-2-chloroethane was fractionated under reduced pressure, the principal fraction boiling at 40° (1 mm.). Identity of the hydroxy ether was checked by molar refraction.

Fifty-four grams (0.3 mole) of the β-hydroxy ether was treated with 73 g. (0.35 mole) of phosphorus pentachloride and 25 ml. of phosphorus oxychloride in a flask equipped with a reflux condenser and stirrer. The reaction was quite vigorous at first. After the initial reaction subsided, the mixture was warmed for 30 minutes, cooled, and poured over cracked ice. After being washed with water and dried over calcium chloride, the product was fractionated at 100 mm. pressure. The principal product boiled at 80° (100 mm.). The refractive index of the compound was 1.3929 at 20°. The boiling point of the chloroether obtained by chlorination of $\mathrm{CH_3CH_2OCF_2CFHCl}$ was 80° (100 mm.) and its refractive index was 1.3935. The structure assigned the compound was therefore $\mathrm{ClCH_2CH_2OCF_2CFHCl}$.

BOULDER, COLORADO RECEIVED OCTOBER 10, 1951

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[17] W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274 (to du Pont) (October 15, 1946).

[CONTRIBUTION NO. 116 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Structure of Alkali Metal-catalyzed Butadiene Polymers[1,2]

BY A. W. MEYER, R. R. HAMPTON AND J. A. DAVISON

The structures of various sodium and potassium-catalyzed butadiene polymers were determined from infrared absorption measurements. All of the polymers had a higher proportion of butadiene in the 1,2-configuration (45–80%) than emulsion polybutadiene (18–23%). Polybutadienes catalyzed by potassium had 15–20% less butadiene in the 1,2-configuration than those in which sodium was the catalyst. When a mixture of sodium and potassium was used, the results were nearly the same as with the potassium catalyst alone. Polybutadienes made at 5° had 10 to 15% more butadiene in the 1,2-configuration than those made at 45°. Diluent type had little or no effect on the structure of the polybutadienes. The butadiene portions of butadiene–styrene copolymers were found to have the same relative proportions of 1,2-, *cis*-1,4- and *trans*-1,4-configurations as the butadiene homopolymers. The second order transition temperature of sodium-catalyzed polybutadiene polymerized at 30° was −45° whereas the 75° polybutadiene had a value of −64°.

Introduction

Considerable information has been obtained concerning the structure of butadiene polymers prepared by the free radical mechanism. The effects of variables such as polymerization temperature and ingredients of the polymerization recipe on the polymer structure were determined.[3,4] It was found that the polymerization temperature governed the resulting structure. Thus with decreasing temperature of polymerization there was an increase in the proportion of *trans*-1,4-butadiene configuration with an accompanying decrease in *cis*-1,4 and little change in 1,2. It has been widely shown that the reduction in polymerization temperature has the effect of increasing tensile strength, abrasion resistance and other properties of the polymer.[5] However the changes in structure obtained by altering the variables of the emulsion polymerization were relatively limited. In order to complete the knowledge regarding obtainable polybutadiene structures, it appeared to be of interest to determine variations in structure produced by polymerizations having a carbanion type of mechanism such as that obtained with alkali metal catalysts.

Previous work has shown[6] that sodium-catalyzed polybutadiene polymers contained about 70% of 1,2-configuration as compared to about 20% for emulsion polybutadiene. These sodium polymers were found to have advantages in processing quality and in balance between flex crack growth and hysteresis properties.[7]

The Government Laboratories at the University of Akron prepared alkali metal-catalyzed polybutadiene and butadiene–styrene copolymers in order to investigate the effects of type of catalyst, polymerization temperature, diluents and rate-retarding modifiers upon the structure and the physical properties of the polymers.[8]

Experimental Procedure and Results

Several series of polybutadienes were made at the Government Laboratories in 8-oz. bottles at 5, 30 and 45°. Three types of catalyst, sodium, potassium and equimolar mixtures of sodium and potassium were used in the following basic formula:

Ingredients	Parts
Monomers	100
Diluent	0–300
Rate modifier	0–1.0
Catalyst	0.16–0.30

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[1] Presented before the Symposium on Synthetic Rubber, Division of Rubber Chemistry of the American Chemical Society, New York, N. Y., September 3–7, 1951.

[2] This work was carried on under Quartermaster Contract W44-109-qm-2030.

[3] E. J. Hart and A. W. Meyer, THIS JOURNAL, **71**, 1980 (1949).

[4] A. W. Meyer, *Ind. Eng. Chem.*, **41**, 1570 (1949).

[5] L. M. White, *ibid.*, **41**, 1554 (1949).

[6] C. S. Marvel, W. J. Bailey and G. E. Inskeep, *J. Polymer Sci.*, **1**, 275 (1946).

[7] A. E. Juve, M. M. Goff, C. H. Schroeder, A. W. Meyer and M. C. Brooks, *Ind. Eng. Chem.*, **39**, 1490 (1947).

[8] W. K. Taft, H. Goldsmith, *et al.*, private communication to the Office of Rubber Reserve.

Illustrative data for the sodium-catalyzed polymers are shown in Table I.

TABLE I

STRUCTURES OF SODIUM-CATALYZED POLYBUTADIENES

Polymer no.	Pzn. temp., °C.	Diluent	Structures by infrared 1,2, %	*trans*-1,4, %	*cis*-1,4, %
1	5	None	74.0	20.0	6.0
2	5	100 pentane	79.5	12.8	7.6
3	5	75 pentane, 25 MCH[a]	77.2	15.3	7.5
30	5	75 pentane, 25 xylene	72.5	21.6	5.9
10	30	None	67.6	24.1	8.3
11	30	100 pentane	66.7	22.1	11.2
12	30	75 pentane, 25 MCH	64.4	23.0	12.6
31		75 pentane, 25 benzene	72.9	16.7	10.4
32	30	75 pentane, 25 xylene	61.0	24.5	14.5
21	45	None	60.9	26.4	12.7
23	45	75 pentane, 25 MCH	59.3	24.8	15.9

[a] MCH = methylcyclohexane.

TABLE II

STRUCTURES OF SODIUM-CATALYZED POLYBUTADIENES

Diluents: *n*-butane and methylcyclohexane; rate modifier: dioxane; polymerization in 5-gallon reactors.

Polymer no.	Pzn. temp., °C.	Structures by infrared, % 1,2	*trans*-1,4	*cis*-1,4	Second order transition temp., *Ts*, °C.
41	30	73.0	17.6	9.4	−45.5
42	40	72.9	17.3	9.8	−48.5
43	50	68.6	17.6	13.8	−54.0
44	60	66.5	18.6	14.8	−55.0
45	75	69.6	17.1	13.2	−63.5

Because of the more violent reactions with potassium and the mixture of sodium and potassium catalyst, smaller amounts of catalyst and greater amounts of diluents were employed. The diluents were pentane, methylcyclohexane, benzene and xylene. The rate-modifier employed for all runs to reduce the polymerization rate was 1.0 part dioxane. Unreacted butadiene monomer was vented from the bottles when no visual increase in viscosity was noted, and methanol was added to destroy any unreacted alkali metal.

Sodium-catalyzed polybutadiene and butadiene-styrene copolymers were prepared by the Government Laboratories in a 5-gal. reactor at 30, 40, 60 and 75° according to the above charge formula. The diluents were *n*-butane, methylcyclohexane, pentane, toluene and xylene. Rate modifiers were dioxane, dodecylamine, piperidine, polyethylene glycol di-(2-ethylhexoate), isopropyl ether and dianisyl disulfide. Data for typical polymers are shown in Table II. The raw polymers were processed at the Government Laboratories by soaking in methanol; then 1.5% phenyl-β-naphthylamine and 2% stearic acid (based on wet polymer weight) were added to the batch on a wash mill or in a pelletizer, followed by drying at 60°.

Samples of the polymers were purified at the United States Rubber Company Laboratories according to the following method: Approximately 2 g. of polymer was dissolved in 100 ml. of carbon disulfide in a 250-ml. flask and shaken overnight. The solution was filtered through a 300-mesh silk screen to remove gel. The filtered solution was poured slowly into 50 ml. of methanol to precipitate the polymer. The liquor was decanted at intervals and replaced with additional methanol. Nearly all of the carbon disulfide was removed at reduced pressure. Then 5 ml. of 0.04% carbon disulfide solution of antioxidant and 2 ml. of 0.1% carbon disulfide solution of *p*-*t*-butylcatechol were added. The polymer was evacuated to dryness at room temperature. About 50 ml. of carbon disulfide was added to give a 4% solution of the polymer. The solution was filtered through a 300-mesh silk screen before making infrared absorption measurements. The concentration of the polymer solution was determined by withdrawing 5 ml. with a calibrated syringe and placing it in a weighed tin. The weight of dry polymer was determined after drying *in vacuo* overnight.

The techniques used in the infrared absorption measurements to determine the amounts of 1,2-, *trans*-1,4- and *cis*-1,4-configurations have been described by Hart and Meyer[8] and Hampton.[9] The method of Hampton which was used for these polymers employs polybutadiene standards.

Polybutadiene exhibits infrared absorption bands at 724, 911 and 967 cm.$^{-1}$, the relative intensities of which vary, depending on the method of polymer preparation. These bands are due, respectively, to *cis*-1,4-polybutadiene, 1,2-polybutadiene and *trans*-1,4-polybutadiene. From measurement of the absorption at the three positions, the isomeric composition of a sample of polybutadiene is calculated by the solution of three simultaneous equations. This method involves the tacit assumption that no other components are present and that the samples had the theoretical total unsaturation, *i.e.*, one double bond per butadiene unit. The measurements for *trans*-1,4-, *cis*-1,4- and 1,2-configurations sometimes yield a total greater than 100%. This may be due to the fact that the total unsaturation of the polymer standards which were used for calibrating the infrared methods was somewhat lower than the values of the present series of polybutadienes. Extremely accurate unsaturation values by chemical methods are required and work of this type is in progress. For the present comparison it is believed that the relative values of the various types of structure are accurately indicated and that the absolute values may be slightly lower than those reported.

The average values of infrared measurements are shown in Table III for polybutadienes catalyzed by sodium, potassium and equimolar mixtures of these two materials at 5, 30 and 45°. At each temperature it was found that polybutadienes catalyzed by potassium had about 15% lower 1,2-configuration than those in which sodium was the catalyst. When mixtures of sodium and potassium were used the results were nearly the same as with potassium catalyst alone.

TABLE III

SUMMARY OF POLYBUTADIENE STRUCTURES[a]

Catalyst	Pzn. temp., °C.	1,2, %	*trans*-1,4, %	*cis*-1,4, %
Sodium	5	76.0	17.3	6.7
Sodium	30	66.5	22.1	11.4
Sodium	45	60.1	25.6	14.3
Potassium	5	54.0	35.6	10.4
Potassium	30	47.6	37.5	14.9
Potassium	45	46.0	37.5	16.5
K–Na	5	55.5	34.4	10.1
K–Na	30	51.4	35.0	13.6
K–Na	45	49.0	37.0	14.1

[a] Average values of bottle runs based on 100% theoretical unsaturation.

As the polymerization temperature for sodium-catalyzed polybutadiene was decreased, the proportion of 1,2-configuration increased and at the same time the proportion of *cis*-1,4 and *trans*-1,4 decreased. Polybutadienes made at 5° had 10–15% more 1,2-configuration than the 45° polymers while the 30° polymers were intermediate. The effects of temperature on structure of polybutadienes catalyzed by potassium and by mixtures of potassium and sodium were similar to those described for the sodium-catalyzed polymers. The type of diluent used had little or no effect on the structure of the polybutadienes (Table I).

The changes in *cis*-1,4-, *trans*-1,4- and 1,2-configuration with polymerization temperature are shown in Fig. 1 to be linear for sodium-catalyzed polybutadienes.

In Fig. 2 it is shown that the changes in isomeric structure with polymerization temperature for the potassium-catalyzed polybutadienes are also linear.

The infrared data for structure of polybutadienes made in 5-gal. reactors are given in Table II. The effects of polymerization temperature on structure are similar to those described above for the sodium polymers made in 8-oz. bottles. However, results show that polybutadienes prepared in 5-gal. reactors do not have identical structure with polybutadienes made in 8-oz. bottles at the same tempera-

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[9] R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).

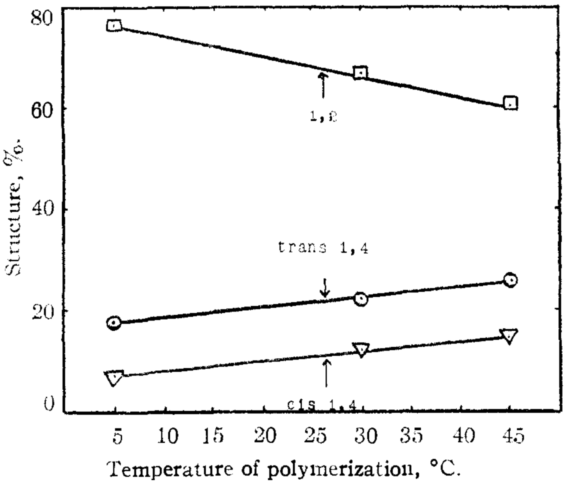

Fig. 1.—Structures of sodium-catalyzed polybutadienes.

ture. It appears that temperatures of polymerization were not as satisfactorily controlled in the 5-gallon reactors.

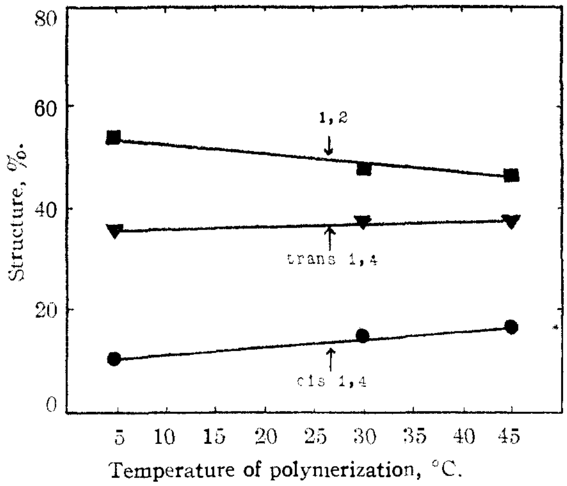

Fig. 2.—Structures of potassium-catalyzed polybutadienes.

An important property of a polymeric material is the second-order transition temperature, T_s. A second-order phase transition is manifested as a change in slope when any of the primary thermodynamic properties of a material, such as volume or heat content, are plotted against temperature; and hence as a discontinuity in the first derivative of these properties. Rubber on being cooled below the transition temperature changes from its normal state of toughness and long-range elasticity to a brittle material with little extensibility.

The values of second-order transition temperature here reported were obtained by plotting volume of the rubbers at various temperatures and noting the temperature at which a change in slope occurs. The second-order transition temperatures, T_s, of the polymers are reported in Table II. Thus, the T_s of the sodium-catalyzed polybutadiene made at 30° was −45° whereas the 75° polybutadiene had a T_s of −64°. In Fig. 3 we have plotted the second-order transition temperature *vs.* % 1,2-structure. The values for free radical-catalyzed polybutadiene previously reported[5] are also included in Fig. 3. Since all points fall on a smooth curve, a direct relationship between % 1,2-structure and T_s is indicated.

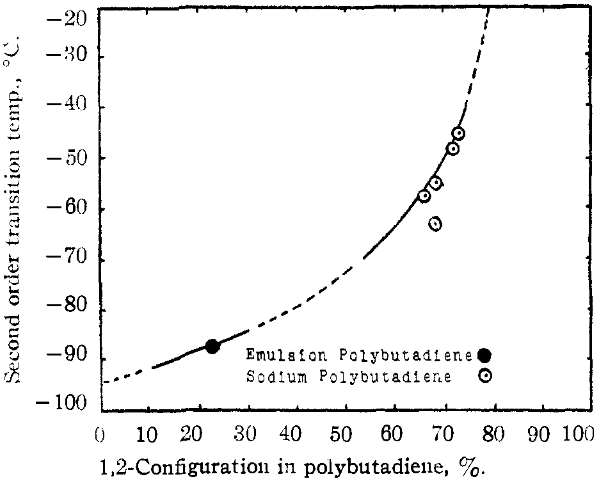

Fig. 3.—Effect of 1,2-configuration upon the second order transition temperature of polybutadiene.

A series of butadiene–styrene copolymers made at 30° at the Government Laboratories were found to have the butadiene with about the same relative proportions of *cis*-1,4, *trans*-1,4 and 1,2 as the butadiene homopolymers but showing a greater degree of variability. This may be due in part to the presence of a variety of diluents and rate-modifiers which influence the rates of the polymerization and possibly the actual polymerization temperatures.

This view is supported by the fact that polymers made at 30° without rate-retarding modifiers had butadiene configurations like those of polymers made at about 45°, *i.e.*, lower % 1,2-configuration.

Passaic, N. J. Received September 7, 1951