the procedure of Steinkopf and Jacob.[19] The solid products crystallized from ethanol–water gave: for 2-methylthiophene m. p. 84–86° (lit. 86°), and for 3-methylthiophene m. p. 33.8–34.0° (lit. 34°). For the chloromercuri derivatives[20] the ethanol-soluble part of the solid products after crystallization from ethanol–water gave: for 2-methylthiophene m. p. 202–204° (lit. 204°) and for 3-methylthiophene m. p. 127–129° (lit. 128–129°). The literature values are quoted from McKittrick.[21]

A 30-cc. sample of each isomer was isolated from rejected distillation fractions by means of the chloromercuri derivatives.[3] The properties of the regenerated products were: 2-methylthiophene b. p. 112.6°, f. p. −63.5°, n^{20}_D 1.5203, d^{20}_4 1.0195, η_{20} 0.717 centipoise; 3-methylthiophene b. p. 115.5°, f. p. −69.4°, n^{20}_D 1.5204, d^{20}_4 1.0216, η_{20} 0.687 centipoise (*cf.* Table I). Examination of the infrared absorption spectra in the range 2 to 15 microns showed the regenerated materials to be equivalent to the corresponding samples isolated physically, with the exception that with the former there was a small amount of mutual contamination. For the regenerated materials, the 2-methylthiophene was found to contain 1 mole % of the 3-methyl isomer; the 3-methylthiophene was found to contain 2 mole % of the 2-methyl isomer. For the physically-purified samples, infrared examination indicated that the purity of each isomer was approximately 99.8 mole %.

In preparing the chloromercuri derivatives there was a noticeable difference in the rates of formation of the solid product. When a mixture of 2-methylthiophene, 3-methylthiophene and thiophene in the molar ratio 1:1:1 partially reacted with mercuric chloride under conditions similar to those described by McKittrick,[21] the portion which had reacted was found by means of infrared absorption spectra to contain the thiophenes in the molar ratio 6:4:1, respectively.

Acknowledgment.—The author expresses his appreciation to Mr. H. E. Rasmussen for supplying the pilot plant products used in this work; to Mr. W. H. Lang for carrying out the distillations; and to Mr. J. G. Ehlers for making infrared examinations of several samples.

Summary

1. The two methylthiophenes have been purified by distillation and the following properties have been determined for each: f. p., b. p. over the range 500 to 900 mm., n_D, d_4 and η at 20, 25 and 30°, η at 0°, specific dispersion at 20°, f. p. depressions for three solutes, and some derived constants.

2. Samples of the two isomers isolated by means of the chloromercuri derivatives showed several properties in agreement with the corresponding properties of the physically-purified specimens.

3. Two crystalline forms of 3-methylthiophene were found; the lower-freezing form has the lower heat of fusion and over the whole range of its existence is metastable with respect to the higher-freezing form.

PAULSBORO, N. J. RECEIVED FEBRUARY 21, 1946

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[19] Steinkopf and Jacob, *Ann.*, **515**, 279 (1935).

[20] Steinkopf, "Die Chemie des Thiophens," Theodor Steinkopff, Dresden, 1941, p. 109.

[21] McKittrick, *Ind. Eng. Chem.*, **21**, 585 (1929).

[CONTRIBUTION FROM THE NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

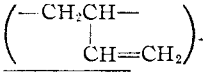
The Mechanism of Modifier Action in the GR-S Polymerization.[1] I

BY H. R. SNYDER, JOHN M. STEWART, R. E. ALLEN AND R. J. DEARBORN

When butadiene and styrene are copolymerized in an aqueous emulsion containing only the monomers, an emulsifying agent, and a peroxidic catalyst the product obtained is an insoluble substance which is difficult to process and is of little value as a rubber. Useful copolymers are obtained by adding to the polymerization system a substance known as a "modifier." In the preparation of GR-S the modifier used is a mercaptan or a mixture of mercaptans. The copolymer produced in the presence of such a modifier is soluble in benzene, and it can be milled and processed much like natural rubber. The present work was undertaken in an effort to determine the nature of the chemical action of the modifier.

It is now generally believed that vinyl polymerizations induced by peroxidic catalysts proceed by a free radical mechanism[2,3,4] in which the essential steps are initiation, propagation, and termination. Peroxide-catalyzed polymerizations of dienes differ from those of simple vinyl monomers in that the steps of initiation and propagation may consist in either 1,4- or 1,2-addition to the diene system, or both 1,4- and 1,2-addition may occur in random fashion. Ozonization studies of polybutadiene indicate that the polymer has a structure of the third type, resulting from both 1,4- and 1,2-addition.[5,6]

At the time of the beginning of the present work two theories were under general discussion as providing possible explanations for the action of modifying agents. In one it was supposed that the modifier acted as a catalyst for 1,4- addition to the diene, or as an inhibitor for 1,2-addition, so that its use resulted in the formation of polymer of essentially linear structure. In the absence of a modifier the polymerization was supposed to yield a product in which a large proportion of the diene units were combined as vinylethylene residues



$\left(\begin{array}{l}-CH_2CH- \\ \qquad | \\ \qquad CH{=}CH_2\end{array}\right)$. The side-chain vinyl groups in

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] (a) Flory, THIS JOURNAL, **59**, 241 (1937); (b) Irany, *ibid.*, **62**, 2690 (1940).

[3] Price, Kell and Krebs, *ibid.*, **64**, 1103 (1942).

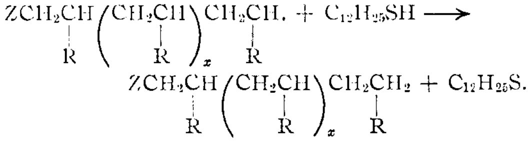
[4] Schulz and Husemann, *Z. physik. Chem.*, **B39**, 246 (1933).

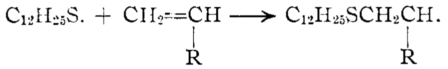
[5] Hill, Lewis and Simonsen, *Trans. Faraday Soc.*, **35**, 1067 (1939).

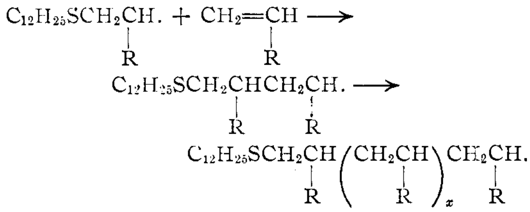
[6] Alekseeva and Belitzkaya, *Rubber Chem. and Tech.*, **15**, 693 (1942).

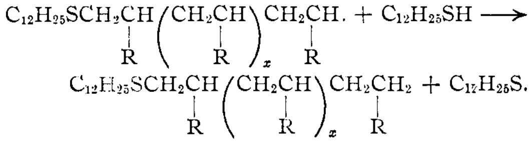
this structure were supposed to be more reactive than the internal double bonds of the structure resulting from 1,4-addition. For example, the side-chain vinyl groups were supposed capable of participation in the polymerization reaction, leading to branched and cross-linked molecules.

In the second theory,[7] it was supposed that the modifier acted as a chain-transfer agent. For example, a molecule of *n*-dodecyl mercaptan may react with one polymer radical to stop its growth, but producing a radical which may start the growth of another. The following equations represent such a chain-transfer process

(1)

$$\mathrm{ZCH_2\underset{R}{C}H\left(CH_2\underset{R}{C}H\right)_xCH_2\underset{R}{C}H. + C_{12}H_{25}SH \longrightarrow ZCH_2\underset{R}{C}H\left(CH_2\underset{R}{C}H\right)_xCH_2\underset{R}{C}H_2 + C_{12}H_{25}S.}$$

(2)

$$\mathrm{C_{12}H_{25}S. + CH_2{=}\underset{R}{C}H \longrightarrow C_{12}H_{25}SCH_2\underset{R}{C}H.}$$

(3)

$$\mathrm{C_{12}H_{25}SCH_2\underset{R}{C}H. + CH_2{=}\underset{R}{C}H \longrightarrow C_{12}H_{25}SCH_2\underset{R}{C}HCH_2\underset{R}{C}H. \longrightarrow C_{12}H_{25}SCH_2\underset{R}{C}H\left(CH_2\underset{R}{C}H\right)_xCH_2\underset{R}{C}H.}$$

(4)

$$\mathrm{C_{12}H_{25}SCH_2\underset{R}{C}H\left(CH_2\underset{R}{C}H\right)_xCH_2\underset{R}{C}H. + C_{12}H_{25}SH \longrightarrow C_{12}H_{25}SCH_2\underset{R}{C}H\left(CH_2\underset{R}{C}H\right)_xCH_2\underset{R}{C}H_2 + C_{12}H_{25}S.}$$

Kharasch has demonstrated that reactions of the type represented by Equation 2 occur.[7a]

According to this theory, the function of the modifier is to regulate the molecular weight of the polymer. It is possible that it also has an effect on cross-linking, however. For example, in the absence of a chain terminator a reactive polymer radical may add to a double bond in another such radical or molecule, so that the attacked body becomes activated at an internal position, and on further growth yields a cross-linked molecule.

Consideration of the theories and of the equations (1–4) suggests several approaches to experimental tests concerning the mechanism of modifier action. In the first place, if the modifying agent functions by regulating the ratio of 1,4- and 1,2-addition, then it should have no effect upon the polymerization of styrene. However, if the agent acts by the chain-transfer process, then successively increasing amounts of modifier should lead to polystyrenes of successively lower molecular weight. The same general effect of modifier concentration on molecular weight should be observed with butadiene polymers and styrene–butadiene copolymers. Furthermore, according to the chain-transfer theory the group RS- appears in each polymer molecule, except those in which the initiation step involved a radical from the catalyst. If this formulation of the mechanism is correct, then the polymer should contain very nearly one sulfur atom per molecule.

Experimental

A. Polystyrene

1. Bulk Polymerization.—The catalyst, 0.5 g. of benzoyl peroxide, was dissolved in 20 g. of styrene; *n*-dodecyl mercaptan, in amounts varying from 0.1 to 5 g., was added to this mixture in a small Erlenmeyer flask. The flask was then stoppered with a tin-foil wrapped cork and heated in an oven at 60–75° for about twenty hours. At the end of this time, 0.5 g. of hydroquinone was added as shortstopping agent to prevent further polymerization; the mixture was transferred and treated with steam to remove the excess styrene. The polystyrene was then washed well with methanol.

Purification of the polymer was effected by reprecipitation by dropwise addition of a dioxane solution of the polystyrene to a vigorously stirred excess of methanol. Three precipitations were made with each sample. Careful drying of the purified product in a vacuum drying pistol gave a fine white powder.

2. Emulsion Polymerization.—A 2.5% aqueous solution of Ivory soap flakes was used as a stock emulsifying solution. To a 4-ounce bottle was added 20 g. of the 2.5% soap solution and 0.5 g. of potassium persulfate. The *n*-dodecyl mercaptan, which varied in amount from 0.05 g. to 8 g., was dissolved in 10 g. of styrene, and the mixture was added to the polymerization bottle. The bottle was sealed with a screw cap fitted with a tin-foil gasket. The polymerization was carried out by tumbling the bottle in a constant temperature water-bath at 50° for about twenty hours.

After removal of the bottle from the bath, 0.5 g. of hydroquinone was added as a shortstopping agent, and the latex was coagulated in a beaker by means of a saturated sodium chloride solution containing a little sulfuric acid. The sticky polymer was subjected to steam distillation to remove excess styrene and then washed well with methanol. Reprecipitation was effected by dropwise addition of a dioxane solution of the polymer to an excess of methanol. Fine white powders or fibers were obtained after drying in a vacuum pistol.

3. Molecular Weight Determinations.—Cryoscopic molecular weights measured on benzene solutions of the low polymers were reproducible within reasonable limits and are believed to be sufficiently accurate for the present purpose. Viscosity measurements also were made, but less significance is attached to the molecular weights calculated from them. An Ostwald type viscosimeter was used and the molecular weights were calculated in accordance with the Kemp–Peters modification of the Staudinger equation.[8]

The results of these molecular weight measurements are given in Tables I and II.

4. Sulfur Analyses.—The purified polystyrenes were ground into fine white powders and oxidized by the Parr bomb method. Sulfur analyses were made on the resulting inorganic residues gravimetrically, with precipitation of

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(7) At the time of the beginning of this work these theories were under lively discussion at various research meetings of rubber chemists, but the authors were unable to trace their originators. The first written intimation of the chain-transfer mechanism of modification which has come to the authors' attention is in a private communication received by the Office of Rubber Reserve in December 1942, from R. H. Ewart, of the United States Rubber Company, wherein it was noted that the presence of mercaptans in the polymerization mixture reduced the molecular weight of polystyrene, and a similar "chain-terminating" action was anticipated for polymerizations involving butadiene.

(7a) Kharasch, Read and Mayo, *Chem. and Ind.*, **57**, 752 (1938).

(8) Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

TABLE I

BULK POLYMERIZATION OF STYRENE WITH *n*-DODECYL MERCAPTAN AS MODIFIER

Run	Styrene, g.	Dodecyl mercaptan, g.	Benzoyl peroxide, g.	Temp., °C.	Time, hours	Conversion, %	Sulfur content, %	Molecular weight (viscosity)	Molecular weight cryoscopic)	S/mole
1	10	0.05	0.1	90–100	15	80				
2	10	.10	.1	90–100	15	70				
3	10	.20	.1	90–100	15	66		17,950		
4	10	.40	.1	90–100	15	60		10,400		
5	15	.85	.85	60	30	60		9,100		
6	23	1.50	.50	60	22	49.5		....		
7	10	0.80	.80	65	22	40		5,000		
8	10	2.0	2.0	65	22	31.5	5.0–5.5	1,290	920	1.6
9	20	3.5	2.5	65	24	36.4	3.5–3.6	4,000	1100	1.2
10	20	4.2	0.5	60	21	34.0	2.8–3.1		1000	0.97
11	21	1.5	.5	60	21	50	..	....	..	..
12	20	2.0	.5	60	21	45	1.28	2,550	1700	.7
13	20	2.8	.5	60	21	33(?)	1.99	2,000	1650	1.03
14	20	3.5	.5	60	21	37	2.29	925	1200	.86
15	20	4.2	.5	60	21	33.5	..	....	..	..
16	18	2.52	.5	75	17	42.5	1.4–1.75	2500–2700	..	1.2–1.3
17	18	1.45	.5	75	17	57.5	2–2.75	1500–1700	..	1.0–1.3
18	8.1	5.6	1.0	65	20	..	10.64		300	1.0

TABLE II

EMULSION POLYMERIZATIONS OF STYRENE WITH *n*-DODECYL MERCAPTAN AS MODIFIER

Run	Styrene, g.	Dodecyl mercaptan, g.	2.5% soap solution, g.	$K_2S_2O_8$, g.	Temp., °C.	Time, hours	Sulfur content, %	Molecular weight (viscosity)	Molecular weight (cryoscopic)	Ratio S/mole
1	10	0.05	20	0.03	50	18	....	....	....	......
2	10	1.00	20	0.50	50	18	1.1	4400	2800	0.96
3	10	2.6	20	0.60	50	18	1.82–1.91	....	1325–1500	.8–0.9
4	10	2.6	20	0.60	50	22	1.80–1.83	....	1647	.94
5	10	2.6[a]	20	0.60	50	20	0.3	12,975	12,350	1.1–1.2
6	23	6.0	45	0.80	50	18	2.5–2.95	1200–1500	....	1.1–1.35
7	9	5.07	20	1.0	50	22		[b]		1.0

[a] Added stepwise; 0.01 g. at start, 0.02, 0.04, 0.08, 0.16, 0.32, etc., added each hour. [b] Addition compound, $C_6H_5CH_2CH_2SC_{12}H_{25}$, isolated as main product.

the sulfur as barium sulfate and weighing as such in the usual manner.

Sulfur analyses on polystyrenes are given in Tables I and II. Comparison of sulfur analyses was made with the cryoscopic values for the molecular weight in all cases where such values were determined.

5. Cleavage of the Modified Polystyrene with Chlorine and Water.—To a solution of 5 g. of a dodecyl mercaptan-modified polystyrene (molecular weight about 1500) in 50 ml. of chloroform was added 3 ml. of glacial acetic acid. Addition of 20 ml. of water caused the formation of a separate layer, and this mixture was saturated with hydrogen chloride gas. Chlorine was next bubbled slowly through the mixture, the flask being shaken vigorously during this addition and cooled externally tok eep the reaction mixture near room temperature. After saturation with chlorine had been effected, the chloroform layer was separated from the water, free chlorine and hydrogen chloride were removed from it, and the solution was added dropwise to an excess of methanol. Several reprecipitations of the polymer from dioxane solution were made, and it was then analyzed qualitatively for sulfur and chlorine. Tests for sulfur were negative, but those for chlorine were strongly positive. It appeared that cleavage of the polymer had taken place in accordance with the equation:[9] $C_{12}H_{25}\text{-S-Polymer} + 3Cl_2 + H_2O \rightarrow C_{12}H_{25}SO_2Cl + \text{Polymer-Cl} + 4HCl$. In addition some chlorination of the polymer obviously had occurred, judging from the large amount of chlorine present. However, all attempts to isolate any 1-dodecanesulfonyl chloride from the chloroform–methanol solutions were unsuccessful.

Efforts were made to prepare 1-dodecanesulfonamide directly in the reaction mixture, after removal of the free chlorine, by passing gaseous ammonia through the solution. None of the expected sulfonamide could be isolated from the reaction products.

6. Hydrogenolysis of Polystyrene.—A modification of the procedure of Mozingo, Wolf, Harris and Folkers for the cleavage of organic sulfides was used.[10] To a solution of 10 g. of polystyrene (modified with dodecyl mercaptan; molecular weight about 2,000) in 250 ml. of cyclohexane or methylcyclohexane, was added about 200 ml. of *n*-butanol, just short of the amount which would produce cloudiness. After 80 g. of Raney nickel catalyst had been introduced, the mixture was refluxed on a steam cone for six to ten hours. The solution was filtered to remove the nickel and most of the solvent was distilled, leaving a volume of about 100 ml. of solution. This solution was then subjected to steam distillation. The organic layer of the distillate was dried over magnesium sulfate and distilled from a Claisen flask until about 2 ml. remained in the flask. During this time the distillation temperature rose slowly to 117°, the boiling point of *n*-butanol, where it remained constant until near the end of the distillation. The residual 2 ml. of yellow liquid was transferred to a 10-

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[9] Lee and Dougherty, *J. Org. Chem.*, **5**, 81 (1940).

[10] Mozingo, Wolf, Harris and Folkers, THIS JOURNAL, **65**, 1013 (1943).

TABLE III

MODIFIERS WITH TRACER GROUPS IN STYRENE POLYMERIZATIONS

Type of polymerization	Modifier	Modifier, %	Time, hours	Temp., °C.	Sulfur, %	Mol. wt. (sulfur analysis)	Neut. or sapon. equiv.	Mol. wt. by osmotic pressure[a]	Mol. wt. by viscosity
Emulsion	Thioglycolic acid	4.8	18	50	0.25	12,800	19,900	17,000	6,000– 8,000
					0.13	24,600	20,200		
					0.22	14,600			
						(Av. 17,300)			
Bulk	Thioglycolic acid	9.1	40	80	0.12	26,700	28,200	22,000	9,000–11,000
							28,800		
Emulsion	Ethyl thioglycolate	21.6	21.5	50	0.15	21,300	18,600		8,000–10,000
					0.22	14,600	22,600		
						(Av. 18,000)			
Emulsion	Ethyl thioglycolate	16.7	9	50	0.18	18,000	22,900		11,000–16,000
					0.12	26,700	23,600		
						(Av. 22,350)			
Emulsion	Ethyl thioglycolate	13.0	6	50	0.12	26,700			13,000-15,000
Bulk	Thioglycolic acid	10.0		80	0.4–0.8	4,000–8,000	8,500–9,000		

[a] The authors are indebted to Dr. F. W. Banes for these measurements.

ml. modified Claisen flask and distilled in vacuum. After removal of the remaining *n*-butanol at room temperature, there were obtained a few drops of a colorless liquid, boiling sharply at 72–73° at 8 mm. pressure. The refractive index at 25° was 1.4205. These constants are in close agreement with those reported in the literature for *n*-dodecane (b. p. 90.5° (11 mm.)[11]; n^{25}_D 1.41967).[12]

7. **Neutralization Equivalents of Polystyrene Modified with Thioglycolic Acid.**—A weighed sample (about 0.5 g.) of the polystyrene was dissolved in 20 ml. of benzene. The solution was heated to boiling, 5 ml. of absolute alcohol was added, and the mixture was titrated with 0.02 *N* alcoholic sodium hydroxide with phenolphthalein as the indicator. For the blank correction, a corresponding amount of unmodified polystyrene was titrated in the same way. The alcoholic sodium hydroxide was standardized against aqueous hydrochloric acid, and, to compensate for any possible end-point changes due to the use of anhydrous solvents, was restandardized against recrystallized benzoic acid dissolved in benzene-alcohol solution. The normality factor was found to be identical in aqueous and non-aqueous solvents.

The end-points in these titrations were sharp and duplicate results were readily obtained. Results are given in Table III.

8. **Saponification Equivalents of Polystyrene Modified with Esters of Thioglycolic Acid.**—In order to saponify completely the ethyl thioglycolate modified polymers, it was necessary to use a high-boiling medium capable of dissolving the polymer. A mixture of equal parts of toluene and *n*-butanol was found to be satisfactory, and the procedure was carried out as follows:

The sodium butoxide–toluene solution, standardized against potassium acid phthalate, was weighed into a 25-ml. glass-stoppered bottle. A 20-g. portion usually was employed, and, the density of the solution having been previously determined, the volume was calculated to the third decimal place. To this solution a 0.5 g. sample of polymer was added, together with a few drops of water. The stopper was wired down and the bottle placed in boiling water for one to two hours. The solution was then transferred to a 125-ml. Erlenmeyer flask, acidified with standard potassium acid phthalate solution, and the excess acid titrated with standard sodium hydroxide solution.

The method is not ideal, since the end-point is poor and titration of the two-phase system is difficult. The sodium salt of the polymer tends to act as a soap and emulsify the toluene–butanol layer. Blank runs were made in each case on unmodified polystyrene samples. The results are given in Table III.

9. **Molecular Weight Determinations and Sulfur Analysis of Polystyrenes Modified with Thioglycolic Acid and its Derivatives.**—For each sample the molecular weight was determined in a number of ways and the values were compared. Molecular weights were first obtained from the neutralization or saponification equivalents. Secondly, molecular weights were calculated from the percentage of sulfur, assuming one sulfur atom present per polymeric molecule. In two cases osmotic pressure measurements[13] were made and the values of molecular weight obtained by this method agree fairly closely with those obtained from sulfur analysis and neutral equivalents. Viscosity measurements were made on each sample and again proved to be unsatisfactory.

Sulfur analyses were carried out by oxidation of the polystyrenes in a Parr bomb and determination of the sulfur gravimetrically as barium sulfate.

Results of these measurements are given in Table III.

10. **Isolation of the Addition Product, *n*-Dodecyl β-Phenylethyl Sulfide, from Polymerization Reactions.**—Both emulsion and bulk polymerizations of styrene in which over 30% by weight of *n*-dodecyl mercaptan was present yielded mainly a high-boiling oil. This oil was taken up in ether and washed with 10% sodium hydroxide solution, then with water, and dried over sodium carbonate. After removal of the ether, a portion of the oil was fractionally distilled. Most of it distilled as a clear, colorless liquid, boiling at 221–223° under 12 mm. pressure.

To a solution of 5 g. of the crude, dried oil in an acetone–acetic acid mixture was added 5 ml. of 30% hydrogen peroxide. The mixture was allowed to stand for two hours at room temperature with occasional shaking, and the mush of crystals which had formed was then filtered and dried. Three recrystallizations from 50% ethanol gave lustrous, crystalline leaflets, melting at 73–74°. Mixtures of these crystals with authentic *n*-dodecyl phenylethyl sulfoxide melted at 73–74°.

Anal. Calcd. for $C_{20}H_{34}OS$: C, 74.46; H, 10.63; S, 9.95. Found: C, 74.19; H, 10.45; S, 10.64.

11. **Preparation of Reagents. a. Thioglycolic Acid, its Sodium Salt and Esters.**—Thiodiglycolic acid was prepared according to the method of Friedländer and Chevala. The disulfide was not isolated,[13a] but was reduced directly to thioglycolic acid which was redistilled under reduced pressure in an atmosphere of nitrogen (b. p. 86–87° at 3

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(11) Krafft, *Ber.*, **15**, 1698 (1882).

(12) Shepard, Henne and Midgley, THIS JOURNAL, **53**, 1953 (1931).

(13) The authors are indebted to Dr. F. W. Banes for these measurements.

(13a) Friedländer and Chevala, *Monatsh.*, **23**, 750 (1907).

mm.). The sodium salt was prepared by neutralizing the acid with the calculated amount of sodium carbonate, precipitating the salt by the addition of alcohol, and drying with ether.

The ethyl ester was prepared by the ordinary esterification with absolute alcohol and a trace of sulfuric acid. The octyl ester was prepared by refluxing the acid and *n*-octyl alcohol in dry benzene with a small amount of *p*-toluenesulfonic acid. Water was extracted from the mixture as it was formed. The ester was washed with sodium carbonate, and distilled twice under reduced pressure in a atmosphere of nitrogen. The boiling point was 124° at 4 mm. pressure.

b. 11-Mercaptoundecanoic Acid.—A solution of 10-undecenoic acid in toluene to which a small amount of benzoyl peroxide had been added was treated with hydrogen bromide at 0° until saturated. The 11-bromoundecanoic acid crystallized when the solution was cooled to −10°, and it was recrystallized from chloroform. The pure bromo acid (m. p. 50–51°) was converted to the mercapto compound by refluxing with thiourea in alcoholic sodium hydroxide. Acidification of the solution yielded nearly pure 11-mercaptoundecanoic acid. After several recrystallizations from alcohol and ligroin, the melting point was 45°. Cohen reports 47°.[14]

c. *n*-Dodecyl β-Phenylethyl Sulfoxide, $C_{12}H_{25}SOCH_2CH_2C_6H_5$.—A solution of 5.1 g. (0.025 mole) of *n*-dodecyl mercaptan and 1.44 g. (0.025 mole) of potassium hydroxide in 40 ml. of hot ethanol was prepared, and 4.62 g. (0.025 mole) of β-phenylethyl bromide was added dropwise to the stirred, hot solution. Potassium bromide precipitated during the course of the reaction. The mixture was refluxed for a half hour after addition of all the bromide; it was then diluted with water and the solution was extracted with ether. The ether solution was washed with 10% sodium hydroxide solution, then with water, and dried over sodium carbonate.

The crude sulfide obtained by evaporating the ether was dissolved in 50 ml. of acetone and 10 ml. of glacial acetic acid. To this solution was added 6 ml. of 30% hydrogen peroxide, and the oxidation was allowed to proceed at room temperature overnight. Lustrous, crystalline leaflets were obtained, which, after two recrystallizations from 50% ethanol, melted at 73.5–74.0°.

12. Polymerization of Styrene in the Presence of Diisopropyl Xanthogen Disulfide.—Bulk polymerizations with this modifier were effected in the same way as those with dodecyl mercaptan, except that the reactions were carried out at the steam-bath and the time of polymerization was twenty-four hours. Emulsion polymerizations were effected in the same way as those with the mercaptan modifier, except that hydrogen peroxide was used as the catalyst. Details of the experiments are given in Tables IV and V.

Table IV

Bulk Polymerization of Styrene with Diisopropyl Xanthogen Disulfide as Modifier

Trial	Styrene, g.	Benzoyl per-oxide, g.	Modifier, g.	Molecular weight[a]	Sulfur analyses, %	Sulfur/mole
1	4.9	0.05	0.05	7170	..	..
2	4.85	.05	.10	2650	..	..
3	4.75	.05	.20	2400	2.5	1.87
4	4.55	.05	.40	1110	..	..
5A	9.50	.10	.40	2305	1.17	0.84
5B				2570	1.17	0.94
6A	9.60	.20	.20	3000	1.82	1.70
6B				4650	1.82	2.64
7	9.60	.20	.20	3490	1.65	1.80
8	9.40	.20	.40	4640	2.50	3.6 (?)
9	9.50	.10	.40	3100	..	..

[a] Molecular weights were determined from viscosimetric measurements, using the Kemp–Peters equation,[8] with the exception of 5B and 6B, which were measured cryoscopically.

Table V

Emulsion Polymerizations of Styrene with Diisopropyl Xanthogen Disulfide as Modifier[a]

Trial	Styrene, g.	H_2O_2 (30%) ml.	Modifier, g.	Molecular weight[b]	Sulfur analyses, %	Sulfur/mole
1	20.0	1.33	0.40	7400	2.49	5.75 (?)
2	20.0	0.66	.20	6600	0.985	2.03
3	20.0	.66	.40	5000	1.20	1.88
4	20.0	.66	.80	3700	1.52	1.75
5	20.0	.66	1.60	2600	2.60	2.09
6	20.0	.66	3.20	[c]	..	..

[a] All polymerizations were run in 40 g. of 2.5% soap solution at 50° for twenty-four hours. [b] Molecular weights by cryoscopic method. [c] No polymer was obtained.

B. Polybutadiene

1. Polymerization of Butadiene in the Presence of *n*-Dodecyl Mercaptan.—Polybutadiene was prepared only by the emulsion method, with 2.5% aqueous solution of Ivory soap flakes as the stock emulsifier. The procedure for a typical run was: Into a 4-ounce bottle was weighed 20 g. of the 2.5% soap solution and 0.10 g. of potassium persulfate, usually as a solution in 3 ml. of distilled water, was added. The bottle was chilled in an ice-salt mixture and, when the contents had solidified, the *n*-dodecyl mercaptan, varying in amount from 0.05 to 8 g., was added. Finally 10 g. of liquid butadiene was weighed in, and the bottle was sealed with a screw cap having a tinfoil gasket over a soft rubber base. The polymerization was effected by tumbling the bottle in a constant temperature water-bath at 50° for about twenty hours. The latex was then removed from the bottle and vented of excess butadiene, 0.1 g. of hydroquinone was added, and the polymer was coagulated with a dilute sodium chloride–sulfuric acid solution.

The sticky gums obtained from the polymerization reactions were washed well by treating them with steam. Most of the water was removed by washing with methanol. After one reprecipitation from benzene solution by the addition of methanol, the polymers were extracted in a Soxhlet thimble for eighteen hours with toluene–ethanol azeotrope. The resulting gums were dried, first in an oven at 75°, and then in a vacuum drying pistol.

2. Determination of Molecular Weights.—The low molecular weight polybutadienes were sticky gums and were very difficult to handle. Results obtained in molecular weight determinations were rather unsatisfactory. Cryoscopic measurement was the only method available since no constant had been determined for polybutadiene for use in the Kemp–Peters equation.[8] Benzene was used as the cryoscopic solvent. Results of these determinations are given in Table VI.

3. Sulfur Analyses.—Since the low molecular weight polybutadienes were gums, they could not be obtained in the finely divided form essential for oxidation by the Parr bomb method. A wet oxidation method was used, following essentially the procedure described by Cheyney.[15,16]

About 0.5 g. of polymer was weighed accurately into a 500-ml. Erlenmeyer flask. A fresh zinc oxide–nitric acid mixture was prepared by adding 10 g. of zinc oxide to 50 ml. of concentrated nitric acid, and 15 ml. of this solution was added to the sample in the flask. The flask was covered with a watch glass and allowed to stand for several hours at room temperature to ensure thorough wetting of the sample. About 15 ml. of technical fuming nitric acid

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(14) Cohen, *J. Chem. Soc.*, 593 (1932).

(15) Cheyney, *Ind. Eng. Chem., Anal. Ed.*, **15**, 165 (1943).

(16) The authors are indebted to Dr. G. D. Sands for these analyses.

TABLE VI

EMULSION POLYMERIZATIONS OF BUTADIENE WITH DODECYL MERCAPTAN AS MODIFIER

Run	Butadiene, g.	2.5% soap solution, g.	Dodecyl mercaptan, g.	Dodecyl mercaptan, %	$K_2S_2O_8$, g.	Time, hours	Temp., °C.	Conversion, %[a]	Sulfur analyses, %[b]	Molecular weight cryoscopic	*S*/mole
1	10	20	0.00	0.00	0.1	20	50	30			
2	20	35	0.10	0.5	.09	12	50	46.5	0.18–0.19		
3	10	20	0.51	5.1	.25	20	50	70			
4	10	20	1.25	10.87	.25	20	50	50			
5	10	20	1.62	13.6	.35	16	50	0			
6	10	20	0.75	6.8	.35	16	50	80	0.9–1.01	2300	0.72
7	10	20	0.75	6.8	.35	18	50	80	.97–1.13	2100	.72
8	10	20	1.00	8.8	.35	18	50	74.0	0.95	2200	.65
9	10	20	0.75	6.8	.35	16	50	50	0.68	2500–2900	.5–0.6
10	10	20	.25	2.2	.10	20	50	90	0.75	2000	.47
11	10	20	.40	3.9	.10	20	50	90	0.68		
12	10	20	.085	0.84	.00	20	50	0.00			
13	20	40	2.0	9.8	.50	20	50	..	1.4–1.8		
14	10	20	6.8	41.0	.50	16	50	..	10.03		
15	10	20	8.5	46	.10	20	50	..			

[a] Based on weight of polymer obtained. [b] The authors are indebted to Dr. G. D. Sands for these analyses.

was then added and the flask was whirled to prevent ignition of the polymer during oxidation. When solution was complete, 5 ml. of saturated aqueous bromine was added, and the solution was slowly evaporated on a hot plate. During the evaporation, small amounts of potassium chlorate were added to the boiling mixture. Evaporation was carried to dryness, and the residual salts were baked until all the nitrates were decomposed, as indicated by the absence of brown fumes. The residue was dissolved in dilute hydrochloric acid, and the solution was analyzed for sulfur, either by gravimetric determination as barium sulfate, or by the volumetric procedure of Luke described in the experimental section of the following report on the sulfur analysis of GR-S.

Comparison of the sulfur analysis with the cryoscopic molecular weight gives the ratio of sulfur atoms per polymer molecule.

The results of these determinations are given in Table VI.

4. Addition Compounds of Butadiene and *n*-Dodecyl Mercaptan.—When *n*-dodecyl mercaptan was employed in amounts of 40% or more of that of the butadiene in polymerization reactions, the product was a heavy oil. The oil from one polymerization mixture, which had been charged with 10 g. butadiene, 8.5 g. of *n*-dodeycl mercaptan, and 0.1 g. of potassium persulfate, was washed well with methanol and then taken up in ether and dried over magnesium sulfate. After removal of the ether, the oil was distilled in an all-glass apparatus incorporating a small modified Claisen flask. No sharp fractionation could be effected with this apparatus, and the boiling point rose steadily from 120 to 220°, where distillation was stopped. That this boiling range is indicative of a mixture was supported by cryoscopic molecular weight determinations made on two arbitrary fractions. A fraction boiling at 120–150° at 5 mm. pressure had an average molecular weight of 238; while a second fraction, boiling at 155–200° at 5 mm. pressure, had an average molecular weight of 307. These values correspond roughly to molecular weights of addition products from one mole of dodecyl mercaptan and one and two moles, respectively, of butadiene.

The higher boiling fraction contained 9.62% sulfur. This compares favorably with the theoretical value of 10.34 per cent. sulfur present in the addition product of two moles of butadiene and one mole of dodecyl mercaptan.

5. Cleavage of Butadiene-dodecyl Mercaptan Addition Product to 1-Dodecanesulfonyl Chloride.—The oil from a polymerization reaction which had been charged with 10 g. of butadiene and 6.8 g. of *n*-dodecyl mercaptan was washed well with methanol, taken up in ether and dried over magnesium sulfate. After removal of the ether, the oil was distilled at 5 mm. pressure. The boiling point rose fairly steadily from 120 to 180°, where the distillation was stopped. A fraction of 1 ml. was taken at 160–161° and a sulfur analysis was made on this liquid. It contained 10.03% of sulfur, which compares favorably with a theoretical value of 10.34% for a structure containing two moles of butadiene and one of dodecyl mercaptan.

About 0.7 g. of this liquid fraction, boiling at 160–161° at 5 mm. pressure, was dissolved in 10 ml. of glacial acetic acid. A little water was added and chlorine gas was bubbled slowly through the solution. This follows the method of Lee and Dougherty[9] for the oxidative cleavage of organic sulfides. The reaction mixture was kept at about room temperature by cooling the flask externally with cold water. When the solution had become saturated with chlorine, it was poured into a beaker filled with crushed ice. An oily precipitate was collected, dried, and recrystallized several times from methanol. The resulting crystals melted at 42–43°. Sprague and Johnson report the melting point of 1-dodecanesulfonyl chloride as 42.5°.[16a]

To a solution of 0.2 g. of the sulfonyl chloride in 10 ml. of ethanol was added 5 ml. of concentrated aqueous ammonia, and the mixture was placed on a mechanical shaker for two hours. It was then refluxed for fifteen minutes, and finally poured into 25 ml. of ice water. The white solid precipitate was dissolved in 10% sodium hydroxide solution. This solution was filtered and then acidified to reprecipitate the sulfonamide. One recrystallization from methanol gave a compound melting at 93–94°. Sprague and Johnson[16a] report the melting point of dodecanesulfonamide as 94.5°.

6. Ozonization of a Butadiene–Dodecyl Mercaptan Addition Compound.—A sample of the oil having a molecular weight of 307 and a sulfur content of 9.62%, and believed to be mainly a mixture of the isomers resulting from the addition of one mole of *n*-dodecyl mercaptan to two moles of butadiene, was examined.

A solution of 4.15 g. of the oil in 100 ml. of chloroform was ozonized.[16b] After removal of the chloroform, the ozonide was cleaved with 100 ml. of 5% hydrogen peroxide. The aqueous solution of the cleavage product was distilled to a residual volume of about 5 ml. The distillate was diluted to 250 ml.

Aliquot portions of the distillate were analyzed for total

(16a) Sprague and Johnson, THIS JOURNAL, **59**, 1837 (1937).

(16b) The authors are indebted to Dr. R. J. Gander for the ozonization.

formic acid by a modification of the method of Reid and Weihe.[17] In this method of analysis the formic acid is oxidized to carbon dioxide by means of an acetic acid solution of mercuric acetate. The carbon dioxide is determined by absorption by Ascarite. The amounts from two portions corresponded to 0.0059 and 0.0060 mole of carbon dioxide from the original sample of oil ozonized. This indicates that about 22.4% of the butadiene units in the addition product are present as vinylethylene residues arising from 1,2-addition. With other samples of the oil, values as high as 32% were found. The range is almost the same as that (23–36%) found by the application of the same ozonolysis and analytical techniques to GR-S.[18,19]

C. Hydrogenolysis of a Butadiene–Styrene Copolymer

A copolymer was prepared from 40 g. of a mixture of butadiene and styrene (3–1 by weight) in the presence of a g. of dodecyl mercaptan; the emulsion polymerization technique described above in connection with polybutadiene was employed. The polymer was washed once with water and twice with methanol. To ensure complete removal of any unchanged mercaptan, the polymer was dissolved in benzene and precipitated by addition to a large excess of methanol, and it was finally extracted with acetone in a Soxhlet apparatus. The sulfur content of the dried material was 0.80–0.83, and the viscosimetric molecular weight was 4600.

A 20-g. sample of the purified polymer was dissolved in 300 ml. of cyclohexane and butanol (about 150 ml.) was added to the point of incipient precipitation. About 75 g. of Raney nickel was added and the mixture was heated on a steam cone for twelve hours. The mixture was treated as described above in connection with the hydrogenolysis of polystyrene, yielding about 1 g. of an oil which on redistillation gave 0.5 g. of pure dodecane, b. p. 114–115° (34 mm.) (lit.,[11] 114° (30 mm.)), $n^{25}\text{D}$ 1.4188 (lit.[12] 1.41967).

Anal. Calcd. for $C_{12}H_{26}$: C, 84.61; H, 15.39. Found: C, 84.70; H, 15.50.

Discussion

The molecular weight of polystyrene formed by either bulk or emulsion polymerization in the presence of *n*-dodecyl mercaptan is inversely proportional to the mercaptan concentration, and the polymers contain approximately one atom of sulfur per molecule (sections A-1 to A-4, Tables I and II). Although the attempted cleavage of the mercaptan residue from a modified polymer by the action of chlorine was not successful (section A-5), the isolation of dodecane by hydrogenolysis over Raney nickel catalyst (section A-6) and the agreement of sulfur content with carboxyl or carbalkoxyl content in polymers prepared in the presence of carboxy- or carbalkoxy-mercaptans (sections A-7 to A-9, Table III) show that mercaptan modifiers are incorporated into the polymers. The less extensive studies with diisopropyl xanthogen disulfide as a modifier (section A-12) show that the inverse relationship between modifier concentration and molecular weight also obtains with this modifier.

Polybutadienes of low molecular weight, prepared in the presence of dodecyl mercaptan, were less satisfactory materials for study than similar polystyrenes. However, the progressive change in physical state, from rubber-like materials through sticky semi-solids to viscous oils, with increasing modifier concentration indicates a decrease in molecular weight with increase of modifier. In view of the experimental difficulties in the determination of the molecular weights and sulfur contents of these polymers the agreement between the observed value of about 0.6 sulfur atom per molecule and the theoretical value of 1.0 is reasonably good (sections B-1 to B-3, Table VI). The isolation of pure dodecane from the products of hydrogenolysis of a butadiene-styrene copolymer (section C) shows that the mercaptan modifier enters the copolymer molecule. The fraction composed of one molecule of dodecyl mercaptan and two molecules of butadiene (section B-4 to B-6) is of especial interest because it represents the simplest possible modified polybutadiene, and any effect which the modifier might have in directing the mode of reaction of butadiene (as, for example, by repressing 1,2-addition) should be easily detected. Attempts to separate pure compounds from this fraction were unsuccessful, and attempts to prepare sulfoxides, which might have been separable, gave explosive peroxides. However, the ozonolysis of the fraction (section B-6) shows that the relative content of 1,4- and 1,2-butadiene residues is essentially the same as that of GR-S prepared in the presence of very much less modifier; thus it appears unlikely that the modifier has any effect on the mode of reaction of butadiene.

All the observations made in this study are in agreement with the predictions of the chain-transfer theory of modifier action.

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[17] Reid and Weihe, *Ind. Eng. Chem., Anal. Ed.*, **10**, 271 (1938).

[18] Marvel, Rabjohn, Lawson and Bryan, University of Illinois, private communication.

[19] Marvel, Rabjohn and Lawson, University of Illinois, private communication.