Polyalkylene Sulfides Containing Silicon. XI*

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As a continuation of earlier work^{1,2} in this laboratory, a variety of polyalkylene sulfides containing silicon have been prepared in an emulsion system. Burkhard³ has obtained low-molecular weight liquid polymers from the reactions of diallyldimethylsilane and tetramethyldiallylsiloxane with ethylene bis-thioglycolate in solution. Since the preparation of polyalkylene sulfides in emulsion has usually been carried out in acidic emulsions. there was some question whether the diallyldimethylsilane would be cleaved in the fashion described by Sommer, Tyler, and Whitmore.⁴ Therefore, a series of emulsion polymerizations of diallyldimethylsilane and hexamethylenedithiol were performed in emulsions which were buffered to various pH values with the acetate buffer system described by Marvel and Nowlin.⁵ The results show that the highest molecular weight polymers, as

TABLE I

EMULSION POLYMERIZATION OF HEXAMETHYLENEDITHIOL AND DIALLYLDI-METHYLSILANE IN BUFFERED EMULSIONS

Polymer No.	Monomers mixture ^a (g.)	Emulsion ^b pH	Activator ¢ (ml.)	Temp. (°C.)	Yield ^d (%)	Inherent ^e viscosity
66	4.42	3.05	1.0	30.0	85	0.328
67	4.42	3.95	1.0	30.0	85	0.425
68	4.42	5.00	1.0	30.0	84	0.410
69	4.42	6.00	1.0	30.0	81	0.390
70	4.42	6.90	1.0	30.0	78	0.334
71	4.42 ·	3.05	1.0	30.0	85	0.445

^a An equimolar mixture of hexamethylenedithiol and diallyldimethylsilane.

^b Buffered with 0.01 molar acetate buffer.
^c Prepared by dissolving 4.42 g. of ammonium peroxydisulfate, 2.21 g. of sodium bisulfite, and 0.22 g. of cupric sulfate pentahydrate in 100 ml. of distilled water which had been redistilled through an all-glass apparatus.
^d Calculated after one reprecipitation.

^e Measured in chloroform after one reprecipitation at 25° (0.4 g. for 100 ml. solvent).

After 11 and 44 hours of tumbling 0.5 ml. of fresh activator solution of composition described in (c) was added.

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	Method	B.	ងចើស៊	BEN	S E R	ΣΩ	щ	E Table con
IENES	Yieldh (%)	80	81 79 85	81 83 84	81 83 79	22	83	69
NE WITH D	Inherent ^ø vis.	0.305	$\begin{array}{c} 0.204 \\ 0.244 \\ 0.520 \end{array}$	0.219 0.294 0.310	0.211 0.262 0.130	0.107	0.211	0.205
POLYMERIZATION OF DIMETHYL BIS-(3-MERCAPTOPROPYL)SIL	Polymer structure	CH,	E (CH ₂) _s i(CH ₂) ₁ S ₃ . CH ₄ 	$E CH_2 - CH - (CH_2)_2 - CH - CH_2 - S - (CH_2)_3 - Si - (CH_2)_4 - S - S - S - S - S - S - S - S - S - $	$ \begin{array}{c} \mathbb{E} \left(\mathrm{CH}_{2} \right)_{*} - \left(\mathrm{CH}_{2} \right)_{*} - \mathrm{S} - \left(\mathrm{CH}_{2} \right)_{*} - \mathrm{Si} - Si$	$E (CH_2)_1 - CH_2)_2 - CH_2)_2 - CH_2 - CH_2)_3 - Si - (CH_2)_3 - S - Si - (CH_2)_3 - S - Si - (CH_2)_3 - S - S - Si - (CH_2)_3 - S - S - S - S - S - S - S - S - S - $	CH ₃) - CH-(CH ₂), - S-(CH ₂), - Si-(CH ₂), - S - Si-(CH ₂), - S - Si-(CH ₂), - S - Si - (CH ₂), - S - Si - (CH ₂), - S - (CH ₂), -	он "Сн.
TABLE II.	Diene	DADMS	DADMS DADMS BMA ^b	BMA BMA DAPA	DAPA DAPA DAPa	DAP	DAC	DAC
	No.	127	$128 \\ 129 \\ 129 \\ 129 \\ 129 \\ 129 \\ 129 \\ 129 \\ 120 $	130 131 132	133 134 135	136	138	139

54

C. S. MARVEL AND H. N. CRIPPS

Polymer structure	Inherent ^{θ} vis.	Yield ^A (%)	Method	
CH4	0.339	87	E	POI
$[_{2})_{6}$ -S-(CH ₂) ₈ - \dot{S}_{1} -(CH ₂) ₈ -S \exists "				LYA
CH_3 BMA = bimethallyl. ^e DAPA = 0.0'-diallylphenyl acetate. ed in chloroform after one reprecipitation. ^h Calculated after ^k E = emulsion polymerization.	^d DAP = $0,0'-c$ one reprecipita	iiallylphenol. tion. ^é B =	• DAC = • bulk poly-	LKYLENE
MERIZATION OF TETRAMETHYLDI-(3-MERCAPTOPROPYL	SILOXANE WI	TH DIENES		E SULFI
Polymer structure	I	aherent ^a viscosi	ity Yield ^b	DE
CH3 CH8		0.222	83	so
$E(CH_2)_6 - S - (CH_2)_3 - Si - O - Si - (CH_2)_3 + CH_2)_3$				CONT
ĊH, ĊH,				AII
CH ₃ CH ₃ CH ₃ CH ₃		0.201	81	NIN
E CH2-CH-(CH2)2-CH-CH2-S-(CH2)2-Si-0-Si-(CI	I₂)₃—S∃ "			G S
cH ₃ cH ₃				ILIO
CH ₃ CH ₃ CH ₃		0.215	84	CON
$E(CH_2)_3 - \dot{S}_1 - (CH_2)_3 - S - (CH_2)_3 - \dot{S}_1 - 0 - \dot{S}_1 - (CH_2)_3 - S]_a$. X
				11

TABLE II (Continued)

Polymer structure CH3 Diene BA/

No. 140 E (CH₂)₆—S—(CH₂)₈—Si—(CH₂)₈—S] "

 CH_3 • DADMS = diallyldimethylsilane. • BMA = bimethallyl. • DAPA = 0.0'-diallyl diallylcarbinol. ¹ BA = biallyl. • Measured in chloroform after one reprecipitation. ^h merization. ¹ S = solution polymerization. ^k E = emulsion polymerization.

TABLE III, BULK POLYMERIZATION OF TETRAMETHYLDI-(3-MEI **Polymer structure** Diene

> No. 151

 $E (CH_2)_6 - S - (CH_2)_3 - Si - 0 - Si - (CH_2)_3 - 3$ CH₃ CH₃ ĊH₃ ĊH₃ Biallyl

 $\begin{array}{ccc} CH_{3} & CH_{3} & CH_{3} & CH_{3} \\ & & & \\ E \left(CH_{2} \right)_{3} - Si - \left(CH_{2} \right)_{3} - S - \left(CH_{2} \right)_{3} - Si - 0 - Si - 0 \\ & & \\ CH_{3} & CH_{3} \end{array}$ Diallyldimethyl-silane 153

Bimethallyl

152

^a Measured in chloroform after one reprecipitation. ^b Calculated after one reprecipitation.

indicated by inherent viscosity measurements, were formed when the emulsions were buffered to pH values in the region of 3.0 to 5.0 (see Table I). Although this experiment does not conclusively preclude any hydrolysis of the diallyldimethylsilane, it does show that the best polymers are formed under the conditions which have been established by earlier workers in this laboratory for the preparation of other polyalkylene sulfides.⁵

The emulsion polymerization of tetramethyldiallylsiloxane with hexamethylenedithiol was unsuccessful due to the failure of the tetramethyldiallylsiloxane to emulsify under the conditions normally employed for the preparation of polyalkylene sulfides. Therefore, it was of some interest to determine if the introduction of thiol groups into diallyldimethylsilane would improve the emulsification of this monomer. The above objective was accomplished by the addition of thioacetic acid to diallyldimethylsilane and hydrolyzing the resultant dithiolester to the dithiol with aqueous sodium hydroxide. See equations (1) and (2).

$$(CH_2=CH-CH_2-)_2Si(CH_3)_2 + 2CH_3-C-SH \longrightarrow O \\ (CH_3-C-S-(CH_2-)_3)_2Si(CH_3)_2 \quad (1)$$

 $(CH_3 - C - S - (CH_2)_2)_2 Si(CH_3)_2 + 2NaOH \xrightarrow{(aq)} (CH_3)_2 Si[(CH_2)_3 SH]_2 + 2CH_3 CO_2Na \quad (2)$

In subsequent emulsion polymerizations of dimethyl bis-(3-mercaptopropyl)silane with a variety of dienes, an improvement in the stability of the latices was usually observed. However, in the emulsion polymerization of diallyldimethylsilane with dimethyl bis-(3-mercaptopropyl)silane, extensive precoagulation was observed. This phenomenon was apparently due to the high percentage of silicon in the resultant polymer.

A number of polyalkylene sulfides containing silicon were prepared using bulk, solution, and emulsion polymerization techniques. The polymers derived from diallyldimethylsilane are summarized in Table II. The results indicate that bulk polymerization produces the highest molecular weight polymers.

Tetramethyldiallylsiloxane was transformed into the corresponding dithiol by the method described for the preparation of dimethyl bis-(3mercaptopropyl)silane. In view of the results obtained in the polymerization of dimethyl bis-(3-mercaptopropyl)silane with various dienes, this new dithiol was polymerized using only the bulk polymerization technique. The results of these polymerizations are summarized in Table III. The silicon-containing polyalkylene sulfides were heavy oils which were very tacky.

We wish to thank the Chemical Division of General Electric Company for generous samples of diallyldimethylsilane and tetramethyldiallylsiloxane which were used in this investigation.

EXPERIMENTAL

Materials

The hexamethylenedithiol, biallyl, bimethallyl, o,o'-diallylphenol, o,o'-diallylphenyl acetate, and diallylcarbinol have been described previously.⁶ These materials were purified by distillation prior to being used in the polymerizations.

Diallyldimethylsilane (General Electric Company): This was distilled under reduced pressure before use. The portion which boiled at 59-60° (42 mm.), n_D^{20} 1.4410, was used in the polymerization experiments. Burkhard³ reported that this material boiled at 68° (50 mm.), n_D^{20} 1.4409.

Water: Distilled water was redistilled through an all-glass apparatus before use in these polymerizations.

Thioacetic acid: Thioacetic acid (Eastman Kodak Company, practical grade) was distilled through a Podbielniak Heligrid column at atmospheric pressure. The fraction used in this investigation boiled at 85-86°, n_D^{20} 1.4635.

Dimethyl bis-(3-mercaptopropyl)silane diacetate: 50 ml. of purified cyclohexane and 22.2 g. (0.058 mole) of diallyldimethylsilane were placed in a flask equipped with a stirrer, reflux condenser, dropping funnel, and thermometer. Then 24.5 g. (0.322 mole) of thioacetic acid was added dropwise at such a rate that the temperature of the reaction mixture never exceeded 85°. After being stirred for two hours, the cyclohexane and excess thioacetic acid were removed by distillation under reduced pressure. The dithiol ester boiled at 127.5-129.5° (0.35 mm.), $n_{\rm D}^{20}$ 1.5068. The yield was 36.4 g. (79%).

Anal. Calcd. for C12H24O2S2Si: C, 49.27; H, 8.27. Found: C, 50.08; H, 8.32.

Dimethyl bis-(3-mercaptopropyl)silane: A solution of 9.5 g. (0.232 mole) of sodium hydroxide in 50 ml. of water and 20 ml. of 95% ethanol was placed in a 300-ml. flask equipped with a stirrer and reflux condenser. 34 g. (0.116 mole) of dimethyl bis-(3-mercaptopropyl)silane diacetate was added and the mixture was heated under reflux with vigorous stirring for 1.5 hours. The reaction mixture was cooled and the upper layer was separated and combined with two 50-ml. benzene extracts of the aqueous layer. After drying the benzene solution with 3.0 g. of anhydrous magnesium sulfate, the benzene was removed by distillation under reduced pressure. The dithiol was then distilled under reduced pressure through a 4-in. column. The dithiol boiled at 66-67° (the yield was 70.5%). In another experiment this dithiol was prepared in 78% yield from thiolacetic acid and diallyl-dimethylsilane without isolating the intermediate dithiolester.

Anal. Calcd. for C₈H₂₀S₂Si: C, 46.10; H, 9.67; S, 30.77. Found: C, 46.35; H, 9.56; S, 31.00.

Tetramethyldi-(3-mercaptopropyl)siloxane diacetate: A mixture of 25.0 g. (0.116 mole) of tetramethyldiallylsiloxane and 20 ml. of purified cyclohex-

ane was placed in a 200-ml. flask equipped with a stirrer, reflux condenser and dropping funnel. Then 22.0 g. (0.263 mole) thiolacetic acid was added dropwise at such a rate that the mixture refluxed gently. After being stirred for five hours, the cyclohexane and excess thiolacetic acid were removed by distillation under reduced pressure. The dithiolester was separated, dried, and distilled under reduced pressure through a one-foot column. The dithiol ester boiled at 125–127° (0.15 mm.); n_D^{20} 1.4816. The yield was 28 g. (66%).

Anal. Calcd. for $C_{14}H_{30}S_2O_8Si_2$: C, 45.86; H, 8.25; S, 17.49. Found: C, 45.86; H, 8.01; S, 17.23.

Tetramethyldi-(3-mercaptopropyl)siloxane: A solution of 10 g. (0.25 mole) of sodium hydroxide in 50 ml. of water and 75 ml. of 95% ethanol was placed in a 500-ml. flask equipped with a stirrer and reflux condenser. 25 g. (0.06 mole) of tetramethyldi-(3-mercaptopropyl)siloxane diacetate was added and the mixture was stirred vigorously for nine hours under a nitrogen atmosphere. The reaction mixture was heated under reflux for 0.5 hour, cooled and acidified to a pH of 5.5–6.0 with 20% hydrochloric acid. The upper layer was separated and combined with a 20-ml. cyclohexane extract of the aqueous layer. The cyclohexane solution was dried over 2.0 g. of anhydrous magnesium sulfate, and the cyclohexane and excess thiolacetic acid were removed by distillation under reduced pressure. The dithiol boiled at 87–89° (0.25 mm.), n_D^{20} 1.4739. The yield was 17.0 g. (63.5%).

Anal. Calcd. for C10H20OS2Si: C, 42.47; H, 9.25. Found: C, 42.11; H, 8.68.

Emulsion Polymerization of Hexamethylenedithiol and Diallyldimethylsilane in Buffered Emulsions

1% aqueous solutions of MP-189-EF⁷ were buffered to various pH values using the 0.01 M acetate buffer described by Marvel and Nowlin.⁵ 5 ml. (4.42 g.) of an equimolar mixture of hexamethylenedithiol and diallyldimethylsilane was added to a 4-oz. screw-capped bottle containing 50 ml. of the buffered emulsifier. Then 1 ml. of a solution prepared by dissolving 4.42 g. of ammonium peroxydisulfate, 2.21 g. of sodium bisulfite, and 0.22 g. of cupric sulfate in 100 ml. of water was added, and the bottles were capped and shaken vigorously before being placed in a 30° constant temperature bath. After being tumbled end-over-end for seven days, the latices were coagulated with 20 ml. of alum coagulant. (The alum coagulant was prepared by dissolving 100 g. of potassium aluminum sulfate dodecahydrate in a mixture of 100 ml. of concentrated hydrochloric acid and one liter of distilled water.) The polymers were reprecipitated by dissolving them in 20 ml. of chloroform and then pouring the chloroform solutions into 200 ml. of methanol with stirring. After the reprecipitated polymers were dried in a vacuum desiccator for 10-24 hours at 0.1 mm., the yields and viscosities were determined. The viscosities were determined in chloroform by the use of the equation, $[\eta] = (2.303/c) \log (t/t_0)$, where c is the concentration of the polymer in grams per 100 ml. of solvent and t and t_0 are the times in seconds for the solution and pure solvent respectively.

Emulsion Polymerization of Dimethyl bis-(3-mercaptopropyl)silane with Various Dienes

Essentially the same procedure as described for the above polymerizations was employed. In this case the emulsifier employed was buffered to a pH of 3.5. The polymers were isolated and purified as described above. The polymerization time was four days.

Solution Polymerization of Dimethyl bis-(3-mercaptopropyl)silane with Various Dienes

The appropriate amount of an equimolar mixture of the dimethyl bis-(3-mercaptopropyl)silane and diene was weighed into a 50-ml. quartz flask. 20 ml. of purified cyclohexane was added; the flasks were flushed with nitrogen and then tightly stoppered. After four days of exposure to polychromatic ultraviolet light (Hanovia Type 7420) at a distance of 8-12 in., the contents of the flask was poured into 250 ml. of methanol with stirring. The precipitated polymer was then dried as described for the emulsion polymerizations. The yields and viscosities were determined as described above.

Bulk Polymerization of Dimethyl bis-(3-mercaptopropyl)silane with Various Dienes

The appropriate amount of an equimolar mixture of the dimethyl bis-(3-mercaptopropyl)silane and diene was weighed into a 25-ml. quartz flask. After four days of exposure to polychromatic ultraviolet light, the polymers were dissolved in 20 ml. of chloroform and the chloroform solution was poured with stirring into 250 ml. of methanol. The rest of the procedure was identical to that described for the emulsion and solution polymerizations.

References

(1) For the tenth paper in this series see C. S. Marvel and H. N. Cripps, J. Polymer Sci., 8, 313 (1952).

(2) For earlier references see C. S. Marvel and C. W. Roberts, J. Polymer Sci., 6, 717 (1951).

(3) C. A. Burkhard, J. Am. Chem. Soc., 72, 1078 (1950).

(4) L. H. Sommer, L. J. Tyler, and F. C. Whitmore, J. Am. Chem. Soc., 70, 2872 (1948).

(5) C. S. Marvel and G. Nowlin, J. Am. Chem. Soc., 72, 5026 (1950).

(6) C. S. Marvel and H. E. Baumgarten, J. Polymer Sci., 6, 127 (1951).

(7) MP-18-EF is an electrolyte-free emulsifier which consists of mixed sodium alkane sulfonates. We are indebted to Dr. Stanley Detrick of Jackson Laboratory, E. I. du Pont de Nemours & Co. for this material.

Synopsis

The optimum pH for the emulsion polymerization of hexamethylenedithiol and diallyldimethylsilane was found to be in the region of 3.0 to 4.0. A variety of polyalkylene sulfides containing silicon were prepared using bulk, solution, and emulsion polymerization techniques. All of the polyalkylene sulfides which contained silicon were heavy oily materials which were very "tacky".

Résumé

Le *p*H optimum pour la polymérisation en émulsion de l'hexaméthylènedithiol et le diallylediméthylesilane se situe dans une région de 3.0 à 4.0. Différents sulfures de polyalcoylène, contenant du silicium, ont été préparés en utilisant les techniques de polymérisation en bloc, en solution et en émulsion. Tous ces sulfures de polyalcoyle, qui contiennent du silicium, sont des matériaux huileux lourds qui sont très gommeux.

Zusammenfassung

Es wurde gefunden, dass das pH-Optimum für die Emulsionspolymerisation von Hexamethylendithiol und diallyldimethylsilan im Bereich von 3,0 bis 4,0 liegt. Eine Anzahl von Silikon enthaltenden Polyalkylensulfiden wurde unter Benutzung von Massen-, Lösungs-, und Emulsionspolymerisationstechnik hergestellt. Alle Silikon enthaltenden Polyalkylensulfide waren schwere ölige Substanzen, die sehr klebrig waren.

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