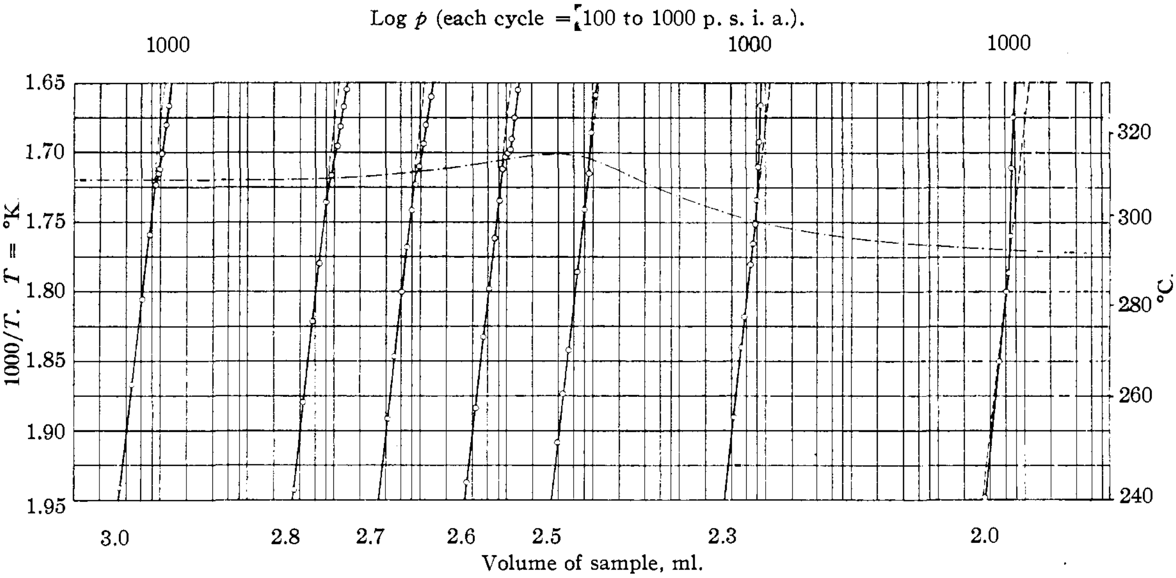

Fig. 6.—Critical point of nitromethane, obtained by interpolating to maximum of critical region: - - - - -, vapor pressure of NM (extrapolated); ——, experimental data; —·—·—, linear plot of points of deviation.

having high critical temperatures. It is apparently limited in accuracy only by the accuracy of the instruments used in measuring temperature and pressure.

The following critical constants were obtained for nitromethane: t_c = 315 ± 1°, p_c = 915 = ±15 p.s.i.a., and d_c = 0.352±0.004 g./cc.

PASADENA, CALIFORNIA RECEIVED OCTOBER 22, 1948

[CONTRIBUTION NO. 253 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO.]

The Structure of Neoprene. II.[1] Determination of End-Groups by Means of Radiosulfur

BY W. E. MOCHEL AND J. H. PETERSON

It is now generally agreed that in the free radical polymerization of vinyl compounds and dienes, fragments of the initiator become combined as end-groups in the polymer molecules.[2] The polymerization catalysts, so-called, are compounds that decompose under polymerization conditions to form free radicals, which in turn become the true, primary initiators. In some cases it has been postulated, on the basis of kinetics studies, that the catalyst first combines with the monomer to produce a complex which subsequently rearranges to an activated molecule,[3] but the structure of the resulting polymer would also involve the catalyst or some fragment as a terminal group. However, not all polymer molecules need have the primary initiator as an end-group. For example, it has recently been demonstrated[4] that the mercaptans used as regulators, or modifiers, particularly in diene polymerizations, are chain transfer agents[5] which likewise become attached as end-groups on the polymer molecules. Other possibilities must also be considered, such as chain transfer with monomer and termination of two chains by mutual interaction without combination[6] to yield additional types of end-groups.

Determination of the end-groups in neoprene (polychloroprene) was therefore undertaken to obtain further knowledge about the structure and formation of this synthetic elastomer. The general purpose chloroprene polymer, Neoprene

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[1] Part I, Mochel, Nichols and Mighton, THIS JOURNAL, **70**, 2185 (1948).

[2] Kamenskaya and Medvedev, *Acta Physicochim., U. R. S. S.*, **13**, 576 (1940); Price and co-workers, THIS JOURNAL, **63**, 2798 (1941); **64**, 1103, 2508 (1942); **65**, 517 (1943); Kern and Kammerer, *J. prakt. Chem.*, **161**, 81 (1942); Bartlett and co-workers, THIS JOURNAL, **65**, 543 (1943); **67**, 812, 816 (1945); Blomquist, Johnson and Sykes, *ibid.*, **65**, 2446 (1943); Pfann, Williams and Mark, *J. Polymer Sci.*, **1**, 14 (1946).

[3] Schulz and Staudinger, *Z. physik. Chem.*, **39B**, 246 (1938); Cuthbertson, Gee and Rideal, *Proc. Roy. Soc. (London)*, **A170**, 300 (1939); Schulz and Blaschke, *Z. physik. Chem.*, **B51**, 75 (1942).

[4] Price and Adams, THIS JOURNAL, **67**, 1674 (1945); Snyder, Stewart, Allen and Dearborn, *ibid.*, **68**, 1422 (1946); Wall, Banes, and Sands, *ibid.*, **68**, 1429 (1946); Smith, *ibid.*, **68**, 2059, *et seq.* (1946); Kolthoff and Harris, *J. Polymer Sci.*, **2**, 41, *et seq.* (1947).

[5] Flory, THIS JOURNAL, **59**, 241 (1937); Mayo, *ibid.*, **65**, 2324 (1943).

[6] Melville, *J. Chem. Soc.*, 274 (1947); Burnett and Melville, *Nature*, **156**, 661 (1945); Flory, THIS JOURNAL, **59**, 251 (1937).

Type GN, is prepared in aqueous emulsion by a free radical mechanism initiated with potassium persulfate; the polymerization is carried out in the presence of elemental sulfur, and the final latex is treated with tetraethyl thiuram disulfide. Thus the product may contain sulfur from any of three different sources. For a study of this type,[7] radiosulfur, S^{35}, was particularly convenient because it could be used to label the different sulfur-containing materials added.[8]

Results and Discussion

Sulfur Modification.—In the polymerization of Neoprene Type GN, elemental sulfur dissolved in the monomer appears to act as a polymerization modifier. Without the sulfur, an insoluble, non-plastic polymer is formed even at low conversion, but polymerization of chloroprene containing 0.5–1.5% of sulfur to approximately 90% conversion followed by treatment with 2.5% of tetraethyl thiuram disulfide yields a soluble, plastic polychloroprene. To investigate the mechanism of this sulfur modification, radiosulfur was used to tag the modifier in a typical Neoprene Type GN emulsion polymerization system[9] and polymer samples, after extraction with acetone to remove free sulfur, were analyzed for combined modifier sulfur by radioactivity assay.

As indicated in Table I the sulfur modifier content, after extraction of the uncombined sulfur, generally increased with conversion both in the original samples, *i. e.*, before treatment with tetraethyl thiuram disulfide, and after the thiuram treatment. This gradual increase in sulfur modifier content was probably due to the increasing sulfur/monomer ratio as the polymerization progressed, rather than to any significant change in mechanism. About 30–60% of the 0.7% of tagged sulfur added to the monomer became combined, but part of that originally combined appeared to be lost during the thiuram disulfide treatment. Statistical analysis of the data for combined modifier sulfur indicated a probability of less than 1% that the differences between untreated and thiuram-treated samples were due to experimental error. Reëxtraction of the samples with acetone for three days failed to change the sulfur contents significantly and this procedure appeared satisfactory for removal of free sulfur.[10]

TABLE I

RADIOSULFUR-TAGGED MODIFIER IN NEOPRENE TYPE GN

Conversion, %	Tagged sulfur content, % Original		Thiuram-treated	
4	0.299	0.303	0.189	0.189
15	.223	.223	.196	.201
27	.250	.309	.201	.201
36	.278	.269	.224	.216
45	.282	.278	.255	.243
54	.296	.299	.264	.273
62	.333	.321	.276	.283
69	.355	.344	.279	.275
75	.396	.400	.325	.314
86	.383	.385	.234	.232

The thiuram disulfide treatment appeared to remove some radiosulfur, but this was shown to be due to an exchange reaction which as yet has not been completely elucidated. The ratio of tagged sulfur, by radioassay, to total sulfur, as determined by chemical analysis, was lower for untreated polymers (average 1.4) than for those treated with tetraethyl thiuram disulfide (average 1.8). Also, the total sulfur content remained relatively constant while the radiosulfur content decreased as the amount of tetraethyl thiuram disulfide added was increased (see Table II).

TABLE II

EFFECT OF TREATMENT ON TAGGED SULFUR CONTENT

Polymer treatment before coagulation, stabilized with	Sulfur, % Tagged	Total	Ratio
Phenyl-α-naphthylamine	0.37	0.51	1.4
1% Thiuram disulfide	.27	.47	1.8
2.5% Thiuram disulfide	.24	.47	2.0
5% Thiuram disulfide	.21[a]	.48	2.3

[a] Standard deviation was only 0.004%.

Sulfur extracted from a thiuram-treated polymer was recrystallized from acetone (m.p. determined was 119.5–120°; original sulfur, m.p. 119–120° and mixed m.p. 118–119°) and found to have a specific activity of 2490 counts per milligram per sixty-four seconds compared to the specific activity of 5025 for the original sulfur. Although sulfur and tetraethyl thiuram disulfide refluxed in boiling acetone or benzene did not appear to exchange appreciably in two hours, a radio exchange did occur when sulfur and the thiuram were heated together in a melt at 95–100° as shown in Table III.

TABLE III

SULFUR-TETRAETHYL THIURAM DISULFIDE EXCHANGE

(Initial $S:S^*$ ratio was 2:1)[a]

Sulfur	Specific activity counts/64 sec./mg.
Original	2609
After 30 min. at 95–100°	2416
Original	2100
After 7 hr. at 95–100°	710
Original	2144
After 16 hr. at 95–100°	744

[a] S^* is used to indicate radioactive tagged sulfur.

Recrystallized thiuram recovered from one of these melts was shown by analysis to be radioactive. On the basis of reported thiuram chemistry[11] it is probable that the sulfur and thiuram

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[7] *Cf.* also Pfann, Salley and Mark, THIS JOURNAL, **66**, 983 (1944).

[8] After this work was under way, a note appeared by Smith and Campbell, *J. Chem. Phys.*, **15**, 338 (1947), describing a similar use of radiosulfur in a study of the persulfate initiation of styrene polymerization. Radiosulfur has also been used recently in mercaptans to measure transfer constants for styrene polymerization, see Walling, THIS JOURNAL, **70**, 2561 (1948).

[9] Collins, U. S. Patent 2,264,173 (Nov. 25, 1941).

[10] A. S. T. M. Designation: D 297-43T.

[11] Levi, *Gazz. chim. ital.*, **61**, 373 (1931); Langenbeck and Rhiem, *Kautschuk*, **12**, 156 (1936).

disulfide react under these conditions to form a thiuram polysulfide in which sulfur exchange occurs and that this polysulfide decomposes again to the disulfide and free sulfur. The recovery of sulfur or thiuram disulfide was never quantitative; there was always a non-crystallizable oil left.

Although it was demonstrated that sulfur exchange with tetraethyl thiuram disulfide can occur in a melt at 95–100°, the conditions used for the neoprene treatment were considerably different and the same mechanism may not hold. The polychloroprene latex (*p*H 11.5–12.0) was treated with a dispersion of the thiuram at 40° for a few minutes, the latex coagulated and, after drying two or three days at room temperature under vacuum, the polymer was extracted with boiling acetone for three days. Furthermore, the indicated exchange in neoprene must involve combined sulfur, not elemental sulfur alone (see Table I), although the sulfur involved may be bound only by coördinate linkages to other sulfur atoms.

Further evidence that there is a reaction between the combined sulfur modifier and the tetraethyl thiuram disulfide was obtained from changes in properties of the polymer. The sulfur-modified polymers prepared in 10 to 90% conversion were insoluble in benzene or chloroform and nonplastic if isolated from the latex without treatment with tetraethyl thiuram disulfide but, after treatment in alkaline emulsion, corresponding polymers were completely soluble and plastic. This solubilization of gel polychloroprene did not occur appreciably unless the sulfur modifier was used. At monomer conversions below 10%, sol polymer of very high intrinsic viscosity was isolated without thiuram treatment but the intrinsic viscosity was decreased by treatment with the thiuram disulfide.

A polychloroprene made in 80% conversion with 0.7% of radioactive tagged sulfur and treated with 2.5% of tetraethyl thiuram disulfide was extracted with acetone to remove uncombined sulfur and fractionated from benzene solution using methanol as precipitant.[1] The results of analyses of the fractions, shown in Table IV, indicate an approximate constancy of combined sulfur from the modifier over a range of molecular weights from 92,000 to 321,000.

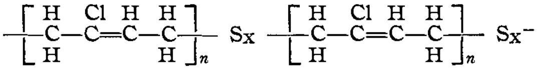
TABLE IV

FRACTIONATED NEOPRENE TYPE GN CONTAINING RADIOSULFUR

Fraction	Weight, g.	$\bar{M}_n$[b]	S*, %	S* atoms/mol.	$\bar{M}$/S* atom	Total sulfur, %
A	2.97	Gel[a]	0.38			
B	6.35	321,000	.31	31.0	10,300	0.59
C	6.79	210,000	.30	20.2	10,400	.37
D	4.85	132,000	.31	12.8	10,300	.36
E	3.18	92,000	.34	9.8	9,400	.40
F	3.03	63,200	.38	7.5	8,400	.46
G	3.54	40,000	.46	5.7	7,000	.75

[a] Fraction gelled during preparation for molecular weight measurements. [b] Number average molecular weight by osmotic pressure measurement.

Obviously the sulfur was not acting as an "end-grouper" like the typical chain transfer agents, since some thirty-one sulfur atoms were combined in each polymer molecule, on the average, in fraction B. On the basis of this evidence the sulfur is believed to be combined essentially as a co-monomer, as has been demonstrated in the case of oxygen.[12] This hypothesis is also in accordance with the observation by Schulz[13] that sulfur is a polymerization inhibitor for styrene, *i. e.*, sulfur reacts with the free radicals to form new, inactive, resonance-stabilized radicals. However, in the case of chloroprene the free radicals ending in sulfur can continue growth. Contrary to the situation in the reaction of oxygen with styrene, the addition of sulfur to the chloroprene free radical appears to be much slower than the growth reaction; consequently, only a small amount of sulfur becomes combined and high molecular weight copolymers are obtained. The number of sulfur atoms combined successively has not been determined but it is probably of the order of 2–6.[14,15] From the chloroprene to sulfur ratio it may be postulated that the structure of Neoprene Type GN before treatment with tetraethyl thiuram disulfide is, in part, the following, where x may be 2 to 6 and *n* is, on the average, 80 to 110 times x (the observed values are higher because of the sulfur exchange)



$$-\left[\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\overset{\text{Cl}}{\text{C}}=\overset{\text{H}}{\text{C}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}\right]_n-\text{S}_x-\left[\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\overset{\text{Cl}}{\text{C}}=\overset{\text{H}}{\text{C}}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}\right]_n-\text{S}_x-$$

(Non-linear linkages of an unknown nature are undoubtedly also present in minor amounts.) The sulfur linkage is believed to be cleaved by a reaction with tetraethyl thiuram disulfide, or its alkaline degradation products, by a mechanism still under investigation. This cleavage yields a soluble, plastic polymer by reducing the average molecular weight below the critical value for gelation.[16] Thus sulfur, unlike mercaptan modifiers, does not directly control molecular weight but yields a product whose molecular weight can subsequently be reduced by the necessary amount to render the gel soluble.

Persulfate Initiation.—To investigate the mechanism of polymerization initiation by persulfates, polychloroprene was prepared using as catalyst, or initiator, potassium persulfate tagged with radiosulfur. The removal of all uncombined persulfate fragments from the polymers was the greatest difficulty in this work. For

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(12) Staudinger, *Ber.*, **58**, 1075 (1925); Staudinger and Lautenschlager, *Ann.*, **488**, 1 (1931); Price, *J. Polymer Sci.*, **1**, 87 (1946); Bovey and Kolthoff, THIS JOURNAL, **69**, 2143 (1947).

(13) Schulz, *Die makro. Chemie*, **1**, 94 (1947).

(14) Farmer and Shipley, *J. Chem. Soc.*, 1519 (1947).

(15) Extraction in hot acetone may remove some bound sulfur. See Kinnear and Harley-Mason, *J. Soc. Chem. Ind.*, **67**, 107 (1948).

(16) Flory, *J. Chem. Phys.*, **46**, 132 (1942).

example, a typical polymer (prepared in 70% conversion with 0.6% of potassium persulfate), differed in its persulfate sulfur content when treated in various ways as shown in Table V.

TABLE V

POLYCHLOROPRENE MADE WITH RADIOPERSULFATE

Successive treatments	Time	Tagged sulfur, %
None (original polymer)	.....	0.102
Mill-washed with 60° water	20 min.	0.056
Mill-wash repeated	30 min.	.054
Extracted with acetone	3 days	.049
Extracted with methanol	3 days	.036
Original extracted with boiling water	3 days	.040
Dissolved in benzene and precipitated with methanol	.....	.0091

After examination of several possibilities, three successive precipitations of the polymers from dilute benzene solution with acetone appeared to be the best procedure for removal of uncombined residues; the tagged sulfur content could thus be reduced to about 0.004–0.005%, with a standard deviation of 0.0006%. The possibility must always be considered that the samples assayed contained residual uncombined inorganic residues from the persulfate. Since rather lengthy treatment of the samples was necessary to obtain constant, reproducible analytical values it may be possible that some persulfate sulfur originally combined was lost by hydrolysis or ester interchange, but this is unlikely at the temperatures involved.[17]

Within experimental error there appeared to be no significant differences in amount of combined persulfate sulfur at different monomer conversion levels.

Fractionation of differently modified polychloroprenes initiated with tagged persulfate, by precipitation from benzene solution with methanol, yielded high molecular weight fractions having relatively high tagged sulfur contents and low molecular weight fractions having little or no combined persulfate sulfur. Results obtained for an unmodified polymer, one modified with 0.7% of elementary sulfur and one modified with 0.30% of dodecyl mercaptan, indicated a difference in the mechanism of initiation (see Table VI). Since these fractionations were carried out in identical manner, it is believed that comparison of the results gives a valid indication of a difference in mechanisms.

TABLE VI

FRACTIONATED POLYCHLOROPRENES MADE WITH TAGGED PERSULFATE

Fraction	Weight, g.	Mol. wt.[a]	Tagged sulfur, %	S*/mole, g.	Mols./S* atom[b]
Unmodified Polymer (5% Monomer Conversion)					
Whole	35.5	......	0.005		
A	8.37	......	.0074		
B	14.72	......	.0017		
C	4.20	1,810,000	.0014	25.3	
D	1.90	......	.0009	....	
E	1.92	525,000	.0006	3.15	10
F	1.35	318,000	.0004	1.27	25
G	1.22	205,000	.0004	0.82	39
H	0.57	124,000	.0005	.62	52
I	.26	......	.0007	....	
Sulfur-Modified Polymer (83% Monomer Conversion)					
Whole	26.2		0.073		
C	6.72	410,000	.0007	2.87	11
D	3.03	218,000	.0015	3.27	10
E	2.16	150,000	.0026	3.90	8
F	1.02	111,000	.0033	3.66	9
G	0.73	85,000	.0028	2.38	13
H	.98	74,000	.0025	1.85	17
Dodecyl Mercaptan-Modified Polymer (69% Monomer Conversion)					
Whole	33.0		0.048[c]		
B	6.30	610,000	.059	360	
C	6.62	365,000	.0004	1.48	22
D	5.53	264,000	.0003	0.80	40
E	1.50	208,000	Nil	....	...
F	3.00	140,000	Nil[d]	(0.085	377)

[a] Molecular weights were determined viscometrically and checked osmotically. [b] Calculated number of polymer molecules per tagged-sulfur atom. [c] Reprecipitation three times from benzene reduced tagged sulfur content to 0.005%. [d] Analysis of a large sample at a long counting period indicated the presence of 0.00006% of tagged sulfur.

The unmodified and sulfur-modified polychloroprenes contained combined sulfur from the persulfate, indicating actual chain initiation by a persulfate fragment, probably SO_4^{-}.[17b] In the case of the sulfur-modified, thiuram-treated polymer, Neoprene Type GN, the radiosulfur assay indicated that from 8 to 17 polymer molecules were formed per combined sulfur atom from the primary initiator and reaction kinetic chain lengths ranged from approximately 1,000,000 to 5,000,000. The formation of 8 to 17 polymer molecules for each primary initiator, presumably by chain transfer with monomer, is not at all unlikely and is of the same order of magnitude as has been reported for other systems.[18]

The unmodified polymer, isolated at very low monomer conversion to obtain a soluble product, contained less persulfate sulfur than the Neoprene Type GN but the amount combined was significantly more than in the case of the mercaptan-modified polymer. Reaction kinetic chain lengths for the unmodified polymer ranged from 5,000,000 to 8,000,000, running through 10 to 52 polymer molecules, for each persulfate sulfur atom combined. Of course, the kinetic chain lengths would be lower if monomer initiation occurred with other free radicals such as hydroxyl, formed by reaction of persulfate with water.

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(17) *Cf.* (a) Hopff and Kern, Trans. by Kline, *Modern Plastics*, **23**, 153 (1946); (b) Bartlett and Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

(18) *Cf.* Schulz and Harboth, *Die makro. Chemie*, **1**, 106 (1947), Melville and Tuckett, *J. Chem. Soc.*, 1211 (1947).

Hydroxyl free radical combination is a possibility which has not been excluded.[17a]

In the case of the mercaptan-modified polymer the final fractions of the polymer contained practically no persulfate sulfur. The amount of persulfate sulfur remaining in fraction F would correspond to a kinetic chain length of approximately 53,000,000, running through 377 molecules, which is considered too high. Chain transfer should not change the reaction kinetic chain length[19] but only the average degree of polymerization. On the basis of available evidence it is proposed that a different initiation mechanism is operating in the presence of the dodecyl mercaptan. It is believed that the potassium persulfate reacts with the dodecyl mercaptan to form free radicals which in turn initiate the polymerization. A possible reaction is

$$K_2S_2O_8 + 2RSH \longrightarrow 2RS\cdot + 2KHSO_4$$

It may be this type of reaction which is responsible for the promoter action of mercaptans, particularly in butadiene polymerization.[20]

Since the high molecular weight fractions always contained large amounts of radiosulfur the possibility must be considered that molecules initiated by persulfate fragments precipitated with the high molecular weight polymer because of reduced solubility. (It is highly improbable that the persulfate-initiated polymer molecules would, on the average, grow to longer polymer chain lengths than others.) It is believed that residual uncombined persulfate fragments, *i. e.*, inorganic sulfates having low solubility in benzene, are carried down by the high molecular weight fractions as they precipitate. The potassium acid sulfate expected would have low solubility in benzene and might need only the nucleus of precipitating polymer to be carried down.

Mercaptan Modification.—To complete this investigation it was considered desirable to examine the action of dodecyl mercaptan, a typical chain transfer agent,[4] in the polymerization of chloroprene. Accordingly, radiosulfur-tagged dodecyl mercaptan was substituted for the sulfur modifier in a typical polymerization system for Neoprene Type GN and the polymer obtained was analyzed, after extraction with acetone.

Typical results, illustrated in Table VII, indicated that the polymers isolated at 10–86% conversions contained on the average more than one mercaptan sulfur atom per polymer molecule. Complete precipitation of these polymers from benzene solutions failed to change the sulfur contents appreciably and a duplicate experiment gave similar values for sulfur content; therefore it is believed that the sulfur remaining was actually combined in the polymer molecules. Note also that there was no significant change in sulfur content as the conversion changed, indicating uniform mercaptan consumption. About 50% of the added mercaptan was combined.

TABLE VII

MERCAPTAN-MODIFIED NEOPRENE (0.30% $C_{12}H_{25}SH$)

Conversion, %	Mol. wt.[a]	S*	S* atoms/ mol.
10	148,000	0.025	1.15
20	175,000	.025	1.36
30	165,000	.025	1.28
41	207,000 (?)	.026	1.68
50	192,000	.019	1.14
59	232,000	.021	1.52
69	161,000	.025	1.26
86	Contained gel	.026	..
		Average	1.34

[a] M_n by osmotic pressure.

Fractionation of the dodecyl mercaptan-modified polymer likewise indicated an average of slightly more than one mercaptan sulfur atom combined per polymer molecule, even after extensive re-extractions and reprecipitations (see Table VIII).

TABLE VIII

FRACTIONATED NEOPRENE MODIFIED WITH 0.30% TAGGED MERCAPTAN (69% CONVERSION)

Fraction	Mol. wt.[a]	S*, %	S* atoms/ mol.	$\frac{\%S^*}{100} - \frac{32}{M}$
Whole	256,000	0.019	1.52	6.5×10^{-5}
A	1,150,000	.010	3.58	7.2
B	890,000	.011	3.05	7.4
C	610,000	.011	2.09	5.7
D	415,000	.013	1.68	5.3
E	312,000	.013	1.26	2.7
F	250,000	.016	1.25	3.2
G	198,000	.019	1.17	2.8
H	165,000	.026	1.34	6.5
I	119,000	.032	1.19	5.0
J	82,000	.013 (?)	0.33 (?)	
K	75,000	.049	1.14	6.2
			Average	5.3×10^{-5}

[a] $\overline{M}_n$ by osmotic pressure.

A polymer was prepared using 1% of the dodecyl mercaptan tagged with radioactive sulfur and was fractionated after three complete precipitations to remove uncombined mercaptan residues. This polymer, of lower molecular weight, and presumably containing fewer side branches per molecule, contained an even greater excess of combined mercaptan sulfur over the theoretical one atom per molecule than the fractions of corresponding molecular weight from the low mercaptan polymer (see Table IX). Similar results were obtained with a product isolated at 25% conversion to reduce the branching still further.

From these results it was apparent that the dodecyl mercaptan was not combined in a simple 1:1 ratio of mercaptan to polymer molecule, as

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(19) Schulz and Blaschke, *Z. physik. Chem.*, **B51**, 83 (1942); Kamenskaya and Medvedev, *Acta Physicochim. U. R. S. S.*, **13**, 586 (1940).

(20) Kolthoff and Harris, *J. Polymer Sci.*, **2**, 41 (1947); Dunbrook, *India Rubber World*, **117**, 357 (1947); Eager and Winkler, *Can. J. Res.* **26**, 527 (1948).

TABLE IX

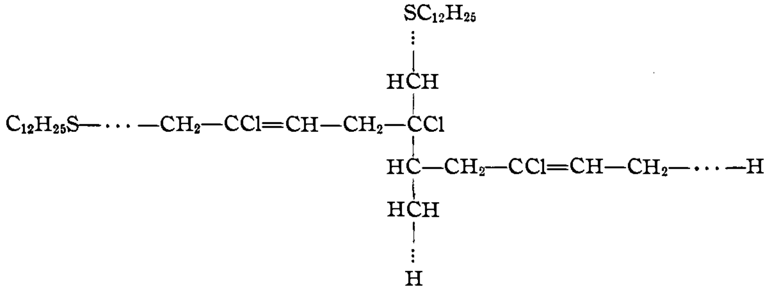
FRACTIONATED NEOPRENE MODIFIED WITH 1.0% RADIOMERCAPTAN (45% CONVERSION)

Fraction	Mol. wt.[a]	S*, %	S* atoms/ mol.	$\frac{\%S^*}{100} - \frac{32}{M}$
Whole	58,000	0.072	1.30	17×10^{-5}
B	160,000	.035	1.75	15
C	130,000	.043	1.74	18
D	103,000	.047	1.51	16
E	74,000	.054	1.25	11
F	59,000	.075	1.38	14
G	40,000	.104	1.30	24
			Average	16×10^{-5}

[a] Viscometrically; C and D checked by osmotic pressure, which indicated $\overline{M}_n$ = 126,000 and 103,000, respectively. Whole polymer by osmotic pressure.

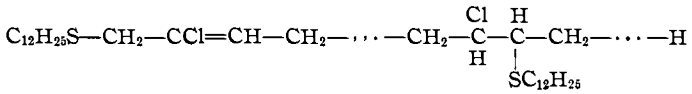
would be expected for linear polymer if only chain transfer were involved.[21] There are three obvious ways in which the mercaptan content could be increased: (1) cross-linking reactions involving growth through double bonds in the polymer chains[22]; (2) mutual combination of two growing chains initiated by RS· to give a maximum of two sulfur atoms per molecule; (3) addition of mercaptan molecules to the double bonds in the polymer chains by the usual free radical mechanism.[23] These reactions would give rise to the structures

(1)



(2) $C_{12}H_{25}S—CH_2—CCl=CH—CH_2—\cdots—CH_2—CH=CCl—CH_2—SC_{12}H_{25}$

(3)



$$C_{12}H_{25}S—CH_2—CCl=CH—CH_2—\cdots—CH_2—\overset{Cl}{\underset{H}{C}}—\overset{H}{\underset{SC_{12}H_{25}}{C}}—CH_2—\cdots—H$$

Mechanism 1 undoubtedly is operative and probably accounts at least in part for the higher-than-average sulfur content of fractions A and B. However, since 1.0% mercaptan yielded polymers containing more sulfur than those made with only 0.30% of the mercaptan it appears that crechanisms 2 and/or 3 are important. Inmeased amounts of mercaptan might well lead to a larger number of growing chains at any given moment and hence a higher probability of termination by mutual combination (mechanism 2); but this mechanism alone cannot lead to the values 3.58 and 3.05 found for fractions A and B of Table VIII. In view of the mild conditions employed for free-radical addition of mercaptans to double bonds of butadiene polymers and rubber,[24] mechanism 3 appears to be the most probable as an explanation of the results observed. The last columns of Tables VIII and IX express the amount of combined sulfur in excess of the theoretical one atom per polymer molecule, reduced to a common molecular weight. The values indicate that, on the average, the second atom of sulfur becomes combined after reaction kinetic chain lengths of 600,000 and 200,000, respectively, for polymerization in the presence of 0.30 and 1.0% of dodecyl mercaptan. The average value for the reduced excess sulfur content for the 1% mercaptan polymers is approximately three times the value obtained when roughly a third as much mercaptan was used. This is strong evidence for a simple mass effect which would be more likely in mechanism 3 than in the others.

Experimental Details

Materials.—The radiosulfur used in this investigation was supplied as irradiated potassium chloride by Clinton Laboratories (now Oak Ridge National Laboratory) and was obtained on allocation from the U. S. Atomic Energy Commission. Carrier sulfur was added and the labeled sulfur isolated by a series of operations involving oxidation to sulfate, precipitation as barium sulfate, reduction to barium sulfide, conversion to hydrogen sulfide and oxidation to free sulfur.[25] It was recrystallized from carbon disulfide before use. This sulfur had an original activity of 1.3×10^6 counts per mg. per 64 seconds.

To prepare potassium persulfate the stock solution of tracer as potassium sulfate plus potassium chloride was converted to potassium hydrogen sulfate and oxidized electrolytically to potassium persulfate,[26] containing radiosulfur.

For the preparation of dodecyl mercaptan containing radiosulfur, the radioactive barium sulfide described above was acidified and the hydrogen sulfide was passed into a methanol solution of sodium methoxide to form sodium hydrosulfide. This was then treated with dodecyl bromide at 120° in a pressure tube for three hours and the radiosulfur-labeled dodecyl mercaptan was isolated and distilled (104–110° (3 mm.)) to yield a product of 96% purity by iodometric titration.

Polymerization.—The polymerizations were carried out in the usual manner[27] at 40°. The sulfur-modified poly-

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(21) Smets and Reiske [*Bull. Soc. Chim. Belg.*, **56**, 159 (1947)] found that the chlorine content of polymethyl methacrylate polymerized in carbon tetrachloride was always slightly less than calculated on the basis of simple transfer.

(22) Medvedev, Chilikina and Klimenkov, *Acta Physicochim, U. R. S. S.*, **11**, 751 (1939); Flory, THIS JOURNAL, **69**, 2893 (1947). Reaction branching as postulated by Medvedev, Koritskaya and Alekseeva, *J. Phys. Chem.* (*U. S. S. R.*), **17**, 391 (1943), would be similar in results.

(23) Kharasch and Fuchs, *J. Org. Chem.*, **13**, 97 (1948).

(24) Kolthoff and Harris, *J. Polymer Sci.*, **2**, 70 (1947); Serniuk, Banes and Swaney, THIS JOURNAL, **70**, 1804 (1948); Cunneen, *India Rubber J.*, **114**, 543 (1948); Naylor, *J. Polymer Sci.*, **1**, 305 (1946).

(25) Clark, Gallo and Lincoln, *J. Applied Phys.*, **14**, 428 (1943).

(26) Henderson and Fernelius, "A Course in Inorganic Preparations," McGraw-Hill Book Co., New York, N. Y., 1935, p. 97.

(27) Walker and Mochel, "Proc. International Rubber Tech. Conf.," London, 1948, Preprint No. 11.

mers were made with 0.7% sulfur. The mercaptan-modified polymers were prepared in the same way, substituting 0.30–1.0% of dodecyl mercaptan for the sulfur. Likewise, for the unmodified polymer no change in the system was made except omission of the modifier. Samples of the latex were removed, treated with 2.5% of tetraethyl thiuram disulfide in emulsion or with 0.5% of phenothiazine and 1.0% of phenyl-α-naphthylamine in emulsion. They were then coagulated with ethanol and dried at room temperature *in vacuo*. Analysis indicated that polymers prepared in this way contained only small amounts of residual soap and other adjuvants.

Preparation of Samples.—As indicated in the Discussion, the polymer samples were extracted or precipitated to remove uncombined sulfur and sulfur compounds. For elemental sulfur and some mercaptan samples the polymers were extracted continuously with acetone or methanol for three to four days in ASTM rubber extractors or Soxhlet apparatus. In other experiments the samples were dissolved in benzene to make 1–5% solutions and the polymer precipitated completely by addition of about 2 volumes of methanol or acetone. Further addition of methanol produced no cloudiness in the clear supernatant liquid.

Radioactivity Assay.—The dry polymer samples were oxidized by the Carius method to obtain a clear solution of sodium sulfate. The sulfate was precipitated as the benzidine salt on special funnels, dried and counted directly with Geiger counters.[28] A control from the labeled sulfur compound under study was always counted at the same time as the unknowns to eliminate the necessity of reliance on decay calculations and to check counter operation with theory based on decay. Sufficient sodium sulfate carrier was added to both control and unknowns to make the sample sizes comparable so that errors due to absorption were eliminated. Furthermore, the control samples were adjusted to roughly the same order of magnitude of counts as the unknowns.

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Summary

By use of radioactive sulfur it has been shown that sulfur-modified neoprene, *i. e.*, Neoprene Type GN, is essentially a copolymer of chloroprene and sulfur in the approximate ratio of 100 chloroprene units per sulfur atom. The sulfur units, possibly disulfides, are cleaved by an alkaline emulsion of tetraethyl thiuram disulfide, so that a gel polymer containing combined sulfur can thus be converted to a soluble, plastic product. The mechanism of this cleavage reaction has not been completely elucidated as yet.

Potassium persulfate, used as initiator for the polymerization of neoprene, appears to be combined with the polymer in Neoprene Type GN in amounts equivalent to 8–17 polymer molecules formed for each sulfur-containing initiator fragment. However, when dodecyl mercaptan is used as modifier, a large proportion of the polymer molecules contain essentially no combined sulfur from the persulfate and it appears that the true initiator is the RS· free radical formed by reaction of the mercaptan with potassium persulfate.

Dodecyl mercaptan used as a polymerization modifier or chain transfer agent, is combined in a greater amount than the one mercaptan per polymer molecule expected on the basis of simple chain transfer. High molecular weight fractions contained 3–4 mercaptan sulfur atoms per polymer molecule and the results suggest that mercaptan addition to the double bonds of the polymer had occurred.

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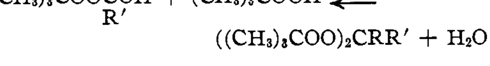
[28] Henriques, Kistiakowsky, Margnetti and Schneider, *Ind. Eng. Chem., Anal. Ed.*, **18**, 349 (1946).

[CONTRIBUTION FROM THE EMERYVILLE LABORATORIES OF SHELL DEVELOPMENT COMPANY]

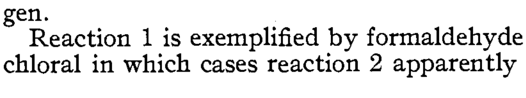
Some *t*-Butyl Hydroperoxide Derivatives of Aldehydes and Ketones

BY FRANK H. DICKEY, FREDERICK F. RUST AND WILLIAM E. VAUGHAN

t-Butyl hydroperoxide combines with aldehydes and ketones to form a series of new compounds which contain either one or two peroxide groups for each carbonyl group. The synthesis is in accord with the equations



$$(CH_3)_3COOH + RR'CO \rightleftharpoons (CH_3)_3COO\overset{R}{\underset{R'}{C}}OH \quad (1)$$



$$(CH_3)_3COO\overset{R}{\underset{R'}{C}}OH + (CH_3)_3COOH \rightleftharpoons ((CH_3)_3COO)_2CRR' + H_2O \quad (2)$$

where R and R′ may be organic radicals or hydrogen.

Reaction 1 is exemplified by formaldehyde and chloral in which cases reaction 2 apparently is of little or no consequence. Rieche[1] mentions the reaction of alkyl hydroperoxides with aldehydes to form hydroxydialkyl peroxides (monoperoxides). However, the ketones investigated in the present work all form liquid bis-(*t*-butylperoxy)-alkanes, as does benzaldehyde.

Experimental

Reactants.—The *t*-butyl hydroperoxide was a commercial product which was purified by steam distillation. After the low boiling fractions had been removed and the distilling temperature had reached 92–93°, the kettle contents were cooled and the phases separated. The upper, hydroperoxide phase, after drying with sodium sulfate, analyzed 78–82%. The ketones and aldehydes were all

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[1] Rieche, "Alkylperoxyde und Ozonide," Theodor Steinkopf, Dresden, 1931.