bumins, purified by these methods, are given.

4. Criteria of the purification achieved are presented.

5. Constants defining the properties of these purified serum albumins are tabulated.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Properties of Polymers as Functions of Conversion. III. Molecular Weights of Bottle Polymerized GR-S[1]

BY F. T. WALL AND L. F. BESTE[2]

Numerous investigations have been carried out on various properties of polymers, such as the intrinsic viscosity, the molecular weight and the composition of copolymers. Much of this work, however, has been directed toward understanding the nature of the final product rather than the nature of the products obtained at different stages of conversion. It is the purpose of this present report to indicate and to interpret the molecular weight changes which occur with increasing conversion for the GR-S system.

The first paper[3] of this series dealt with the theoretical equations by which conversion data might be analyzed. In the second paper[4] the concept of "partial conversion properties" was defined and detailed intrinsic viscosity data were used for illustrative purposes. Although intrinsic viscosity gives some indication about the molecular weight it is felt that the viscosity does not provide a truly reliable index of that quantity. In particular, if one is interested in counting molecules it becomes necessary to determine a number average molecular weight which is usually quite different from that obtained by a viscosity measurement.[5] To obtain a number average molecular weight it is necessary to use some method involving a colligative property of the polymer solution such as its osmotic pressure. In this paper there will be reported the results of three separate studies of osmotic molecular weights of bottle-polymerized GR-S covering wide ranges of conversion.

Partial Conversion Properties

As indicated earlier,[4] if the molecules formed up to a certain stage of a polymerization reaction remain unchanged throughout the remainder of the polymerization, then any subsequent changes in the average or cumulative properties of the polymer can be attributed to the new molecules formed. Actually, since polymer molecules once formed can undergo further reactions, the apparent increment properties often reflect only the net result of a number of simultaneous processes. For this reason we shall employ the term "partial conversion property" to denote an *apparent* property of a polymer increment. "Partial conversion properties" will be denoted by double bars placed over the appropriate symbols. Thus, the partial conversion molecular weight will be indicated by and defined as

$$\overline{\overline{M}} = \mathrm{d}W/\mathrm{d}N \qquad (1)$$

where W is the weight of polymer and N the corresponding number of moles. The average or cumulative molecular weight will of course be given by $\overline{M} = W/N$.

The partial conversion molecular weight is easily computed by the following method. Since $N = W/\overline{M}$, it follows that

$$\frac{\mathrm{d}N}{\mathrm{d}W} = \frac{\overline{M} - W(\mathrm{d}\overline{M}/\mathrm{d}W)}{\overline{M}^2} \qquad (2)$$

From this we see that the partial conversion molecular weight is given by

$$\overline{\overline{M}} = \frac{\overline{M}^2}{\overline{M} - W(\mathrm{d}\overline{M}/\mathrm{d}W)} \qquad (3)$$

The partial conversion molecular weight is important in the study of polymerization kinetics since it is precisely the reciprocal of the net rate of formation of new molecules with respect to conversion.

Experimental

Three series of bottle-polymerized GR-S were investigated. The first two series were polymerized in 4-oz. bottles in triplicate and the last series was polymerized in a 32-oz. bottle from which samples were removed at various times by means of a hypodermic syringe.[6] For all three sets, the polymerization bottles were tumbled end-over-end at 21 revolutions per minute in a bath whose temperature was controlled at 50 ± 0.05° by means of an appropriate thermostat. The charge for the first series was made up according to the following recipe

Material	Parts by weight
Proctor and Gamble SF Flakes	5.25
Potassium persulfate	0.30
Pure dodecyl mercaptan	0.269
Water	180.0
Styrene	27.0
Butadiene	73.0

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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 (first reported October 1, 1945).

[2] Present address: Rayon Department, Technical Division, E. I. du Pont de Nemours and Co., Buffalo 7, New York.

[3] F. T. Wall, THIS JOURNAL, **67**, 1929 (1945).

[4] F. T. Wall, R. W. Powers, G. D. Sands and G. S. Stent, *ibid.*, **69**, 904 (1947).

[5] P. J. Flory, *ibid.*, **65**, 372 (1943).

[6] R. L. Frank, C. E. Adams, J. R. Blegen, R. Deanin and P. V. Smith. *Ind. Eng. Chem.*, in press.

The latex samples obtained at the various conversions for Series I were cooled in ice and diluted to 200 ml. in volumetric flasks. A 50-ml. portion of each was added dropwise to a mixture of 50 ml. of butanol and 10 ml. of salt–acid and the resulting coagulum washed and dried for a conversion determination. For some of the later samples isopropyl alcohol was substituted for butanol.

The recipe for the last two series was as follows

Material	Parts by weight
Proctor and Gamble SF Flakes	5.25
Potassium persulfate	0.30
Pure dodecyl mercaptan	.35
Water	180.0
Styrene	25.0
Butadiene	75.0

Samples for conversion determinations in the last two series were prepared by dropwise addition of the latex to a 0.10% solution of β-naphthol in ether. The remainder of each latex sample was coagulated in absolute alcohol containing a little phenyl-β-naphthylamine.

All of the samples were prepared for osmotic pressure measurements by cutting the dried polymer into small pieces and placing them into thiophene-free benzene in the ratio of 6 g. to 1 liter and allowing the system to stand in the dark from two to six days. The solutions were then filtered through 100-mesh stainless steel screens and the concentrations were determined by evaporation of aliquot portions.

Each sample was precipitated with methanol to remove impurities and extremely low molecular weight polymer. This was done by slowly adding a volume of methanol equal to one-half of the original volume of the solution. After the addition of methanol each sample was allowed to stand in the dark until its supernatant liquid was clear. At this stage the supernatant liquid was siphoned off, its volume measured and the concentration of polymer left in solution determined. The precipitate was washed with methanol and dried in a high vacuum at room temperature for about three hours. It was then dissolved in specially-dried benzene; if the precipitated sample did not dissolve completely it was discarded. The final solution was placed in a volumetric flask and the concentration determined. In every case the concentration was of the order of 0.3 g. per 100 ml. Portions of this solution were further diluted to concentrations equal to 0.7, 0.5 and 0.2 of that of the original solution.

The osmotic pressure measurements were carried out in all-glass osmometers designed by Ewart and French.[7] These osmometers were the same as those employed in an earlier investigation of the molecular weight of GR-S.[8] The membranes were prepared from du Pont 300-gage non-moisture proof cellophane which was swollen in aqueous ammonia.

The measurements were made at about 30° in a thermostat which was maintained constant within 0.005°. The heights of the solution and solvent were read to the nearest 0.005 cm. by means of a cathetometer. From the osmotic rises, properly corrected for capillary rise, the limiting value of the pressure per unit concentration was obtained by the method of least squares. Two or more determinations were carried out at each of the four concentrations for each sample so at least eight and generally twelve points were involved in the curves which were so analysed.

Results and Discussion

The three series of bottle polymerized GR-S will be discussed in the order in which they were studied, although the last series is the most reliable. It should be emphasized that these results are not quantitatively valid for the commercial product which is made under different conditions. The experimental results for the first series are summarized in Table I. In this table are given the polymerization time, the per cent. conversion, the solubility, the intrinsic viscosity of the sample used for osmotic measurements and the number average molecular weight for each sample.

TABLE I
(Series I)

Polymn. time in hours	Per cent. conversion	Per cent. solubility	$[\eta]$	$\overline{M}$
3.5	18.6	100	1.42	35,100
5	31.0	100	1.63	34,600
6.5	41.0	99	1.74	37,100
9.5	65.2	99	2.00	37,300
10.5	70.6	99	2.36	39,300
11.5	74.6	99	3.31	42,200
12.5	77.8	95	2.50	39,750
14	84.2	80	2.31	
19	93.4	48	1.32	

The average molecular weights have been plotted against conversion and the smoothed out curve analysed to give partial conversion molecular weights and related quantities. These results appear in Table II. The values for $\overline{M}$ given in Table II were taken from the smoothed out graph, so they are not identical with those in Table I.

TABLE II
(Series I)

Per cent. conversion	$\overline{M}^{a}$	$d\overline{M}/dW$	$\overline{\overline{M}}$	$dN/dW \times 10^6$
18.6	33,600	370	42,200	2.4
31.0	36,200	125	40,500	2.5
41.0	37,100	526	39,300	2.5
65.2	37,300	111	46,300	2.2
70.6	39,300	1237	−37,000	−2.7
74.6	42,200	0	42,200	2.4

[a] Taken from graph.

The results for the second series studied are given in Tables III and IV. These results are considered somewhat more reliable than those of Series I. Series III is probably the most accurate of all three sets; the corresponding data are summarized in Tables V and VI. In addition the results for this series are plotted in Figs. 1 and 2

TABLE III
(Series II)

Polymn. time in hours	Per cent. conversion	Per cent. solubility	$[\eta]$	$\overline{M}$
3.5	23.5	99	1.75	28,760
5	33.2	99	1.87	30,700
6.5	44.9	99	2.02	36,350
7.5	53.8	100	2.23	38,000
8.5	61.6	100	2.41	37,260
9.5	66.7	99	2.55	44,000
10.5	72.7	98	2.87	47,700
11.5	75.8	92	2.86	49,200
13.5	81.2	86	2.39	42,300

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[7] French and Ewart, *Ind. Eng. Chem., Anal. Ed.*, **19**, 165 (1947).

[8] F. T. Wall, F. W. Banes and G. D. Sands, THIS JOURNAL, **68**, 1429 (1946).

TABLE IV
(Series II)

Per cent. conversion	$\overline{M}^a$	$d\overline{M}/dW$	$\overline{\overline{M}}$	$dN/dW \times 10^5$
23.5	28,800	163	33,160	3.0
33.2	30,700	357	49,970	2.0
44.9	36,350	272	54,690	1.8
53.8	38,000	0	38,000	2.6
63.0	38,750	2166	− 15,360	−6.5
66.7	43,600	884	−123,400	−0.81
72.7	47,700	629	311,000	0.32
75.8	49,200	0	49,200	2.0

[a] Taken from graph.

TABLE V
(Series III)

Polymn. time in hours	Per cent. conversion	Per cent. solubility	$[\eta]$	$\overline{M}$
1.5	8.4	100	0.79	29,200
3	20.6	97	.90	33,200
4.5	29.9	98	1.01	35,400
6.5	43.2	97	1.09	37,000
7	51.2	96	1.16	37,400
8	59.5	99	1.21	36,800
9	66.2	99	1.41	42,800
10	72.2	98	1.77	46,200
11	77.0	97	2.35	48,900
13	84.4	98	2.24	40,700

TABLE VI
(Series III)

Per cent. conversion	$\overline{M}^a$	$d\overline{M}/dW$	$\overline{\overline{M}}$	$dN/dW \times 10^5$
8.4	29,200	466	33,700	3.0
20.6	33,200	266	39,700	2.5
29.9	35,400	167	41,300	2.4
43.2	37,000	83.7	41,200	2.4
51.2	37,400	0	37,400	2.7
60.6	37,100	357	88,800	1.1
61.0	37,250	491	190,600	0.5
61.2	37,350	607	6,065,000	0.016
61.3	37,400	714	−218,000	−0.46
62.0	38,000	1412	−29,200	−3.4
66.2	42,400	849	−130,000	−0.77
72.1	46,700	664	−1,913,000	−0.05
74.0	47,950	652	∞	0
77.0	48,900	0	48,900	2.0

[a] Taken from graph.

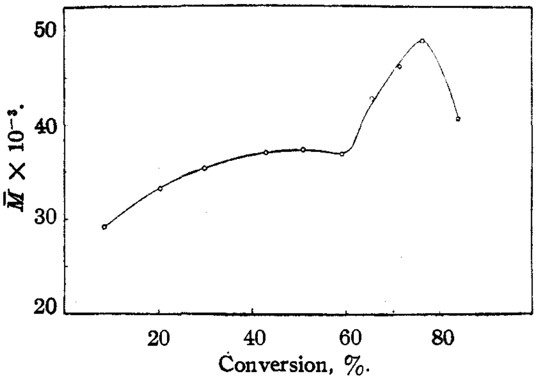

Fig. 1.—Average molecular weight ($\overline{M}$) *vs.* weight conversion for bottle polymerized GR-S.

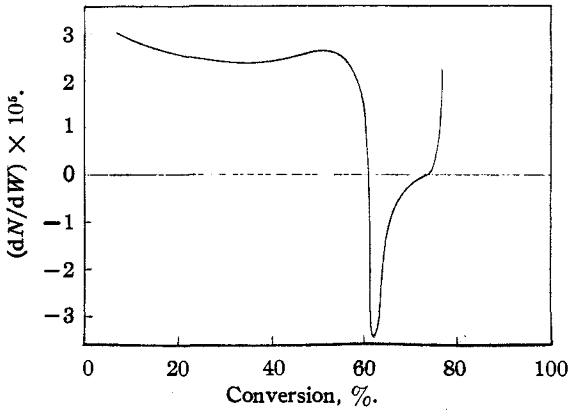

Fig. 2.—Net rate of formation of moles of polymer ($dN/dW = 1/\overline{\overline{M}}$) *vs.* weight conversion.

which show how $\overline{M}$ and $dN/dW(= 1/\overline{\overline{M}})$ depend on conversion. The values of dN/dW instead of $\overline{\overline{M}}$ are plotted in Fig. 2 to keep the interesting parts of the curve on the graph.

It will be observed that the first polymer molecules to form have a relatively low average molecular weight (something less than 30,000) but that with increasing conversion the average molecular weight builds up to about 37,000 in the neighborhood of 60% conversion. According to the chain-transfer theory of modifier activity,[8,9] each polymer molecule should contain the fragments of one mercaptan (modifier) molecule. Therefore it should be possible to compute the number average molecular weight of the polymer from a knowledge of the amount of mercaptan consumed. Mercaptan disappearance experiments by Professor I. M. Kolthoff[10] and co-workers indicate molecular weights very close to those reported here from 0–60% conversion.

Above 60% conversion, however, a remarkable phenomenon is observed. The number average molecular weight increases so rapidly that the partial conversion molecular weight becomes infinite and then negative (at about 61.2% for Series III). At first thought a negative molecular weight would appear to be meaningless and impossible, but when it is realized that the partial conversion molecular weight, $\overline{\overline{M}}$, is just the reciprocal of dN/dW, the interpretation is clear. The rapid increase in average molecular weight is primarily due not to the formation of new large molecules, but rather to cross-linking together of molecules previously formed. The cross-linking process simultaneously diminishes the number of molecules and increases the average molecular weight, thus accounting for the observed results. It should be noted that this proof of cross-linking

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[9] H. R. Snyder, J. M. Stewart, R. E. Allen and R. J. Dearborn, *ibid.*, **68**, 1422 (1946).

[10] Kolthoff and Harris, private communication.

might have escaped notice if the concept of partial conversion properties had not been introduced.

At about 74% conversion the partial conversion molecular weight changes sign again. The reason for this behavior is not absolutely clear since any of several possible factors could cause it. First of all, the nature of the cross-linking reaction might change. Cross-linking is a process which either joins together two distinct molecules or joins together two parts of the *same* molecule. As long as intermolecular cross-linking predominates, a net negative rate of molecule formation can result. Intramolecular cross-linking, on the other hand, does not produce a decrease in the number of molecules. Accordingly the formation of a few new molecules while the second type of cross-linking occurs is consistent with the observed reversal of sign for dN/dW.

Another process which can bring about the change in sign of the partial conversion molecular weight is degradation. Although degradation can occur, it is difficult to specify its extent quantitatively because of the numerous other simultaneous reactions. At about 77% conversion the molecular weight reaches a maximum of about 50,000. The decrease in molecular weight at higher conversions may be due to degradation at least as long as the polymer remains soluble. After gel begins to form it can be argued that the decrease in average molecular weight is due to the removal of the largest molecules as gel, thus leaving only lower molecular weight material to be studied experimentally. When gel formation becomes significant, the partial conversion molecular weights lose much of their meaning.

In addition to all the possible reactions heretofore mentioned, there should be added still another, namely, branching. Branching presumably occurs sooner than cross-linking, but it cannot be detected by partial conversion molecular weight studies. Branching will not alter the ratio of modifier to polymer molecules, and although it can increase molecular weights it cannot give rise to negative partial conversion values. The ways in which branching, cross-linking and degradation can occur have been discussed in some detail by Taylor and Tobolsky.[11]

Summary

Molecular weights of bottle-polymerized GR-S have been determined as functions of conversion. The partial conversion molecular weights are found to be negative between 61 and 74% conversion, thus indicating a net decrease in the number of polymer molecules with increasing weight conversion. This negative rate of molecule formation is attributed to intermolecular cross-linking. Above 74% conversion intramolecular cross-linking and degradation may become important.

[11] H. S. Taylor and A. V. Tobolsky, This Journal, **67**, 2063 (1945).

URBANA, ILLINOIS RECEIVED JANUARY 13, 1947

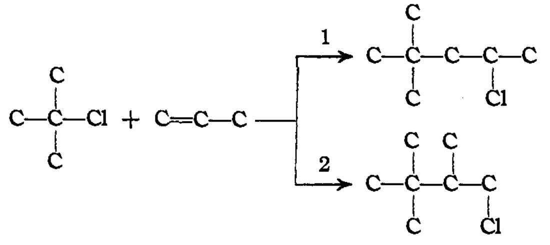
[RESEARCH LABORATORIES DIVISION OF GENERAL MOTORS CORPORATION]

The Aluminum Chloride-Catalyzed Addition of *t*-Butyl Chloride to Propylene

BY VERLE A. MILLER[1]

During the course of a general reaction study made in the search for a method of preparation of triptane (2,2,3-trimethylbutane), higher alkyl chlorides were found in a mixture of *t*-butyl chloride and propylene which had been left in a steel bomb at room temperature for several days. Since less reaction occurred in a glass pressure vessel with steel end-plates, the reaction catalyst may have been iron chloride. This conclusion was in agreement with the work of Schmerling on the catalyzed addition of alkyl halides to ethylene[1a] which was presented at about the same time.

Theoretically, two different methods of addition of *t*-butyl chloride to propylene are possible. According to analogous reactions, the heptyl chloride produced should be that from reaction 1. This has been prepared and characterized by Whitmore and Johnston,[2] but that from reaction 2 has not been described.



This paper presents the study of the structures of C_7 molecules obtained from the addition of *t*-butyl chloride to propylene in the presence of aluminum chloride.

Experimental Procedure

A 500-ml., three-necked flask was fitted with a mercury sealed stirrer, reflux condenser, thermometer and a coarse capillary gas inlet tube which extended well below the halide liquid level. A bubbler containing aqueous sodium hydroxide was inserted between the top of the condenser and a coil trap (which was cooled with acetone and Dry Ice) to serve as a guide for the control of the propylene addition rate.

When the desired reaction temperature was below the freezing point of *t*-butyl chloride, the stirred halide was

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[1] Present address: Firestone Tire and Rubber Company, Akron 17, Ohio.

[1a] L. Schmerling, This Journal, **67**, 1152 (1945).

[2] Whitmore and Johnston, *ibid.*, **60**, 2265 (1938).