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

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In the preceding paper[2] there has been discussed the theory of modifier action in GR-S polymerization. Briefly the theory assumes that certain compounds, such as mercaptans, can act as transfer agents[3] for growing free radical chains. The net effect of this action is to reduce the molecular weight of the polymer and to keep it more soluble. Assuming that chain transfer occurs much more frequently than initiation and termination, it follows that practically every polymer molecule will have incorporated in it one modifier fragment. Experimental support for the theory was obtained by studies on various different polymer systems,[2] which, however, did not include direct measurements on commercial GR-S.

To provide further evidence for the chain transfer-free radical mechanism of polymerization,[3] a number of careful molecular weight measurements and sulfur determinations were carried out on certain portions of GR-S samples. The purpose of these measurements was to find the average number of sulfur atoms per molecule of polymer. If the number found was close to unity, then that would provide further support for the above-mentioned theory.

Several difficulties were encountered in the determination of molecular weights and sulfur contents of GR-S. In the first place, GR-S is highly heterogeneous so it was found desirable to fractionate the material before making the measurements. Secondly, the very low sulfur content in the fractions of interest necessitated the development of special techniques for the quantitative determination of those small amounts of sulfur. Finally, the molecular weights had to be determined osmotically since only number average molecular weights would serve the purpose in mind.

Since an appreciable fraction of each of the GR-S samples investigated was insoluble in benzene and similar solvents, the gel fraction had to be removed if meaningful molecular weights were to be obtained. In addition the very low molecular weight material present in GR-S also had to be removed to make possible significant osmotic pressure measurements on the bulk of polymer. If the low molecular weight material were not removed, the membranes used would have to be so impermeable that osmotic equilibrium could not be attained in a reasonable length of time. Accordingly, the fraction investigated was taken as that portion which was soluble in benzene but insoluble in a mixture consisting of equal volumes of benzene and methanol.

Experimental Procedure

Considerable care had to be exercised in preparing the polymer for osmotic measurements. In particular the effects of heat, light, and long drying had to be avoided. The best results were obtained when the following procedure was adopted.

About 10 g. of GR-S was extracted in the dark at room temperature by cycling acetone through the sample. The extracted sample was dried for nine hours in a vacuum desiccator and then placed in a large Erlenmeyer flask and covered with two liters of C.P. benzene. The polymer was permitted to dissolve by allowing the system to stand for three and one-half days at room temperature. The gel was removed by filtering through an 80-mesh Monel metal screen covered with glass wool.

After removal of the gel, the polymer was subjected to partial fractional precipitation by adding the solution to an equal volume of methyl alcohol. The resulting polymer suspension was then coagulated with a small amount of sodium chloride. Following coagulation the sample was washed with water and with alcohol, after which it was dried in the dark in a vacuum desiccator for nineteen hours. About 1 g. of this material was dissolved in 200 ml. of C.P. distilled benzene, and portions of this solution were diluted for osmotic pressure measurements.

The osmotic pressures were measured by means of glass osmometers[4] immersed in a thermostatically controlled water-bath. The membranes employed were made of no. 300 non-moisture proof cellophane which was treated with 60% zinc chloride solution according to the method of McBain and Stevens[5] for the purpose of swelling the material to the proper permeability. The nature of the membrane depended a great deal on the concentration of the solution in which it was swollen, and many of the membranes had to be discarded because of the improper permeability characteristics. The membranes were sealed to the osmometers by means of polyvinyl alcohol and were kept soft during storage by having them immersed in benzene containing a trace of triethylene glycol and water.

The height of the column of solution above that of the solvent was measured by means of a cathetometer. To make sure that osmotic pressures were really being measured, the level of the solution in the capillary tube was initially set at a point below the equilibrium level, adjustments being made if necessary after observing the early effects. (The system was, of course, allowed to reach temperature equilibrium before any osmotic tendencies were observed.) The level of the solution was then observed as a function of time by means of periodic cathetometer readings. The level would always reach a maximum in the course of several hours, after which it would fall off slowly as a result of diffusion of solute through the membrane. The time required to reach the maximum depended upon the initial difference in heights and upon the porosity of the membrane. When approximate information was available on certain samples, the measurements could be expedited by starting the system near equilibrium. If the falling off of height after the maximum was reached proved to be very rapid, the measurement was discarded. When the rate of diffusion of solute through the membrane was slow, a correction for that diffusion could be applied by extrapolating to zero time, but usually that correction was small enough to be neglected.

(2) Snyder, Stewart, Allen and Dearborn, THIS JOURNAL, **67**, 1422 (1945).

(3) Flory, ibid., **59**, 241 (1937).

(4) The osmometers were similar to those used by Ewart and French. The design was obtained from them through private communication.

(5) McBain and Stevens, J. Phys. Chem., **40**, 1157 (1936).

Measurements were made at several different concentrations for each solution investigated. The equilibrium solution rise was corrected for the capillary rise of the solvent in each case. In analyzing the results, the best quadratic function of the form

$$h = ac + bc^2 \qquad (1)$$

was determined for each sample by the method of least squares. In equation (1), h represents the corrected osmotic rise in centimeters and c the concentration in grams per 100 ml. of solution. With benzene as a solvent at 30.4° (the temperature of the experiments), the molecular weight can be calculated by means of the equation

$$M = \frac{2.96 \times 10^5}{(h/c)_0} \qquad (2)$$

where

$$(h/c)_0 = \lim_{c \to 0} h/c = a \qquad (3)$$

Sulfur was determined in the prepared samples of GR-S by a combination of the methods of Luke[6] and of Cheyney.[7] The procedure involved the complete oxidation of the sample by means of fuming nitric acid, bromine, and potassium chlorate. Excess oxidizing agents were removed by prolonged heating of the solid materials, followed by successive additions of hydrochloric acid and further evaporations to dryness.

The sulfate resulting from the oxidation was reduced by adding some hydrogen iodide reagent, and the hydrogen sulfide generated was distilled into a cadmium chloride solution. An excess of standard 0.01 N potassium iodate solution was added to the latter solution, which was then back titrated with standard 0.01 N sodium thiosulfate solution, using starch as an indicator.

Because of the small amounts of sulfur involved, blank determinations had to be carried out to correct for the sulfur present in the reagents used. Using the best grade of reagents available, blanks amounted to as much as 0.006 milliequivalent of sulfur, which in extreme cases was equivalent to 40% of the total sulfur found by the final titration. This source of error is the most serious in the whole procedure and is the principal cause of uncertainty in the results.

Experimental Results

A summary of osmotic results, molecular weights, sulfur contents and atoms of sulfur per molecule is given in Table I. The values of $(h/c)_0$

TABLE I

Polymer	$(h/c)_0$	Molecular weight	Sulfur, %	Atoms of sulfur per molecule
A₁	8.870	33,300 ⎫	0.071	0.73
A₂	9.100	32,600 ⎭		
B₁	8.510	34,800 ⎫	0.064	0.69
B₂	8.540	34,600 ⎭		
C	5.959	49,740	0.0728	1.13

(6) Luke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 602 (1943).

(7) Cheyney, *ibid.*, **15**, 164 (1943).

were computed by the method of least squares from at least eleven and sometimes as many as sixteen osmotic pressure measurements. Of the results given in Table I, the values for Polymer C are the most accurate, since the greatest precautions were taken in preparing that sample and in carrying out the sulfur analyses.

Discussion

In discussing these results, it should be made clear that the commercial GR-S samples used were among the first ones made in the government program, and accordingly must not be regarded as representing the current product. The particular samples investigated had considerable gel, so the average molecular weight of the soluble portion was low. This was true because gelation preferentially removes large molecules. However, this should not seriously alter the theoretical interpretation to be attached to the results.

It should be recognized that several effects can arise which will bring about deviations from the one-to-one correspondence between sulfur atoms and polymer molecules. First of all, it is possible that radical chains can be terminated by disproportionation or combination, which would have the effect of modification without mercaptan consumption. This process would tend to lower the sulfur content per molecule. Secondly, cross-linking reactions doubtless take place which would tend to increase the number of sulfur atoms per molecule. If cross-linking goes far enough, the molecules so affected will become incorporated into a gel structure which is insoluble. Since the experiments were carried out only on the soluble portion, it is clear that gelation should not affect the interpretation advanced. Only the moderately cross-linked molecules which remain soluble will affect the sulfur–polymer ratio.

The amount of sulfur in the fractions of interest was found to be in the neighborhood of 0.07% with a probable error amounting to about 5 or even 10% of that figure. The precautions which had to be taken for the accurate determination of such small amounts of sulfur were discussed in the experimental section. The osmotic molecular weights varied from 33,000 to 50,000 for the different samples with probable errors equal to about 5%.

From some of the earlier determinations it was calculated that an average of about 0.7 atom of sulfur was present per molecule. The way the early experiments were carried out suggested that the figure 0.7 was experimentally too low, and so more accurate experiments were conducted on a small number of samples. The best experiments indicated 1.1 atoms of sulfur per molecule. Although the figures 0.7 and 1.1 have large probable errors, they are sufficiently close to unity to lend support to the free radical-chain transfer mechanism. Considering the difficulties involved, the figure 1.1 in particular (which was the result of

the most accurate measurements) must be re-
garded as being compatible with theory.

Summary

The chain transfer theory of modifier action has
been tested on commercial GR-S by means of
molecular weight and sulfur content determina-
tions. The number of sulfur atoms per molecule
was found to range between 0.7 and 1.1, to be
compared to the theoretical value of unity. In
view of the experimental difficulties involved, the
results are considered to be in good agreement
with the theory.

The Nitration of Bicyclo[2,2,1]heptane[1]

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In connection with work in this Laboratory on
the mechanism of the vapor-phase nitration
reaction, bicyclo[2,2,1]heptane was treated with
nitric acid in the vapor phase in order to deter-
mine whether or not a bridgehead carbon atom
would be nitrated under these conditions. Na-
metkin and co-workers reported that liquid-
phase nitration of camphane yields no tertiary
derivative.[2]

Procedure.—The hydrocarbon was synthe-
sized by the method of Joshel and Butz as im-
proved by Thomas.[3] A vapor-phase nitration
using 100 g. of it dissolved in 200 ml. of carbon
tetrachloride for convenience of handling, was
made with 1:1 ratio of nitric acid at 400–410° and
atmospheric pressure.[4] The nitro derivatives
were separated from the unreacted materials by
fractional distillation at reduced pressure, stirred
over 10% aqueous sodium hydroxide for 30 hours,
extracted with ether and the ether extract, after
the ether had evaporated, purified by fractional

crystallization and chromatography in ether
solution over Norite. The resulting solid, some-
what waxy like its parent hydrocarbon, melted
sharply at 63°; yield about 50% of nitrated prod-
uct. Tested with the indicator developed by
Davidson,[5] it was found to contain no primary
or secondary nitro group. It is therefore 1-
nitrobicyclo[2,2,1]heptane.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.55; H,
7.86; N, 9.92. Found: C, 59.05; H, 7.9; N,
9.66.

This proves the possibility of nitrating a bridge-
head carbon atom.

The secondary nitro derivatives were regener-
ated by carbon dioxide, but not separated and
identified.

Summary

1-Nitrobicyclo[2,2,1]heptane has been pre-
pared by the vapor-phase nitration of bicyclo-
[2,2,1]heptane, proving the possibility of nitrat-
ing a bridgehead carbon atom.

(1) An abstract of the thesis by R. T. Blickenstaff, submitted to
the Faculty of Purdue University in partial fulfillment of the re-
quirements for the degree of Master of Science, February, 1946.

(2) Nametkin, Dobrovol'skaya and Oparina, *J. Russ. Phys.-
Chem. Soc.*, **47**, 405, 409 (1915).

(3) Joshel and Butz, THIS JOURNAL, **63**, 3350 (1941); Thomas,
Ind. Eng. Chem., **36**, 310 (1944).

(4) For a reference to the general technic employed, see Seigle and
Hass, *Ind. Eng. Chem.*, **31**, 648-650 (1939).

(5) Davidson, *J. Chem. Education*, **19**, 154, 532 (1942).