

overnight. After washing with water and drying, the crude product was distilled, yielding 19.4 g. (33%) of X at 240–242° and 0.05 mm., n_D^{20} 1.4318.

Anal. Calcd. for $C_{60}H_{130}O_{18}Si_4$: Si, 9.58; *MRD*, 325.3; mol. wt., 1172. Found: Si, 9.84, 10.01; *MRD*, 321.7; mol. wt., 1143.

Heptakis-(1,3-dimethylbutoxy)-trisiloxanol (XI).—Eighty-five grams (0.143 mole) of the disiloxanol (IX) was added dropwise with stirring to a cold mixture of 42 g. (0.140 mole) of II and 30 g. of dry pyridine. After an hour 70 ml. of water was added rapidly and stirring was continued for an additional hour. The organic layer was extracted with ether, washed with water, and dried over magnesium sulfate. After removal of ether the crude product was distilled, yielding 75 g. (65%) of XI at 185° and 0.1 mm., n_D^{20} 1.4255.

Anal. Calcd. for $C_{42}H_{92}O_{10}Si_3$: Si, 10.0; *MRD*, 230.8;

mol. wt., 841. Found: Si, 10.5, 10.9; *MRD*, 228.2; mol. wt., 840, 843.

Octakis-(2-ethylhexoxy)-trisiloxane (XV).—Efforts to isolate the trialkoxysilanol derived from 2-ethylhexanol were unsuccessful and this silanol was prepared *in situ* by addition with stirring of 66.7 g. (0.148 mole) of the chlorosilane (XII), over a period of 2 hours, to 2.66 g. (0.148 mole) of water in 100 ml. of dry pyridine. During the next half-hour 24.6 g. (0.074 mole) of bis-(2-ethylhexoxy)-dichlorosilane (XIII) was added, and stirring was continued for an additional half-hour. The reaction mixture was washed with water, dried and distilled. Thirty-five grams (41%) of XV was collected at 260–269° and 0.05 mm., n_D^{20} 1.4428.

Anal. Calcd. for $C_{84}H_{136}O_{10}Si_3$: Si, 7.32; *MRD*, 332.9; mol. wt., 1150. Found: Si, 7.90, 7.92; *MRD*, 329.8; mol. wt., 1111, 1134.

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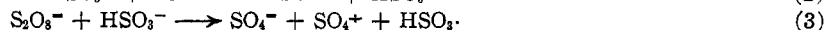
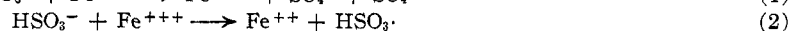
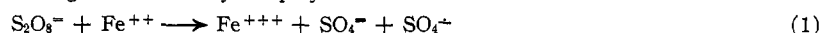
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Tracer Studies of Oxidation-Reduction Polymerization and Molecular Weight of "Teflon" Tetrafluoroethylene Resin

BY K. L. BERRY AND J. H. PETERSON

The objective of this work was to determine the molecular weight of polytetrafluoroethylene. Since the polymer is insoluble and infusible, attempts were made to introduce and determine radiosulfur-containing end groups derived from persulfate initiator. Polymers initiated by persulfate activated thermally or by reaction with Fe^{++} or bisulfite did not contain sulfur from the persulfate. When bisulfite containing radiosulfur was employed in oxidation-reduction initiation reactions with persulfate or Fe^{+++} , polymers with non-hydrolyzable sulfur-containing end groups from the bisulfite were obtained. These results are explained on the basis that the following are the most probable radical-producing reactions in decreasing order of effectiveness for initiating tetrafluoroethylene polymerization.



The translation of radioactive end group determinations to molecular weights is based upon the foregoing view of the initiator reactions and the assumptions (1) that there is no chain transfer or disproportionation in the polymerization, and (2) that termination is by combination of radicals. The number average molecular weights of some relatively low molecular weight polytetrafluoroethylenes are in the range 142,000–534,000.

Introduction

No data on the molecular weight of polytetrafluoroethylene have yet been reported because the insolubility and extremely high melt viscosity of this polymer¹ have precluded determinations by conventional methods. In this paper we report the use of radioactive sulfur in bisulfite and persulfate initiator components for determining end groups and molecular weights of some polytetrafluoroethylenes prepared under various conditions.

Examination of this polymer by end group analysis is singularly informative in view of evidence¹ that there is no branching in the polymer. The results have given additional information on the chemical nature of end groups derived from several initiator systems and on the oxidation-reduction reactions involved in persulfate-bisulfite systems.

Experimental Details

Preparation of S^{35} -Containing Persulfate and Bisulfite.—The radiosulfur used in this investigation was obtained as irradiated potassium chloride from Oak Ridge National Laboratory and was allocated by the U. S. Atomic Energy Commission. Preparation of potassium persulfate containing radioactive sulfur has been described.²

(1) W. E. Hanford and R. M. Joyce, *THIS JOURNAL*, **68**, 2082 (1946).

(2) W. E. Mochel and J. H. Peterson, *ibid.*, **71**, 1426 (1949).

Sodium bisulfite containing radiosulfur was prepared by burning the sulfur (0.1–0.8 g.) in a large excess of oxygen streaming through a heated glass tube, and absorbing the sulfur dioxide in sodium hydroxide solution at 0°. The weighed sulfur sample was placed in a small test-tube which was inserted in the hot tube at a point where the temperature was 250–275°. The sulfur slowly volatilized and burned evenly at the mouth of the test-tube. The gases then traveled through a zone where the maximum temperature was about 550°. The exit gases were bubbled through approximately 0.1 M NaOH solution in the amount calculated on the weight of sulfur to produce NaHSO₃. Some oxidation of SO₂ to SO₃ occurred during combustion, and there was also some oxidation of bisulfite in the solution by oxygen. Recoveries of sulfur as bisulfite, however, were 91 to 96%. The bisulfite was used in the solution as prepared. The solutions were stored at 2–4° under a nitrogen atmosphere, and the bisulfite content determined before each use.

Purity and Handling of Monomer.—Tetrafluoroethylene was purified by distillation under pressure at 4.5 atm. at which pressure the boiling point is –43°. Each batch was analyzed for oxygen, and only material containing less than 10 p.p.m. of oxygen was used. The monomer in the gas phase was stored at approximately 100 lb./sq. in. in a steel cylinder at ambient temperature behind a barricade in an isolated location and piped through a pressure reducing valve to the reactor.

Polymerization.—The apparatus in which polymerizations were conducted comprised a Model A Parr hydrogenation unit³ modified by providing a pressure gage connected to the 325-ml. Pyrex brand glass reaction vessel. The latter was equipped with a glass thermocouple well containing an iron-constantan thermocouple for indicating the tempera-

(3) Manufactured by the Parr Instrument Company, Moline, Ill.

TABLE I
 SULFUR CONTENT OF POLYTETRAFLUOROETHYLENES MADE WITH INITIATORS CONTAINING RADIOSULFUR

Experi- ment no.	Initiator system	Adducts	Polymeri- zation temp., °C.	Sulfur content of the polymer, wt., %	\bar{M}_n/S
1	$K_2S_2O_8$	65	Inactive
2	$K_2S_2O_8$	5 mg. precipitated iron powder	0	Inactive
3	$K_2S_2O_8 + NaHSO_3$	2 mg. $FeSO_4 \cdot 7H_2O$ (=2 p.p.m. Fe^{++} in system)	26	Inactive
4	$K_2S_2O_8 + NaHS^*O_3$	2 mg. $FeSO_4 \cdot 7H_2O$ (=2 p.p.m. Fe^{++} in system)	25	0.025	123,000
5	$K_2S_2O_8 + NaHS^*O_3$	1 g. borax	36	.012	267,000
6	$NaHS^*O_3$	50 mg. $FeCl_3 \cdot 6H_2O$	25	.045	71,000

ture of the reaction medium, an external close-fitting steel cup having a viewing port and a nichrome ribbon electrical heating element wrapped around the outside of the cup. This cup also served as a shield and the whole unit was additionally shielded to guard against the possibility of damage or injury from fragments of the glass reactor in the event of an explosion. The temperature of the reaction medium was determined potentiometrically and controlled either manually or automatically to about $\pm 2^\circ$ by altering the voltage on the heating coil. In experiments conducted at 0° , the reaction bottle was set in an aluminum cup of crushed ice. Rate of polymerization for the types of initiation studied was found to be a function of degree of agitation, so this variable was kept constant by employing in all experiments the same bottle, charge volume, and amplitude and frequency of shaking.

The polymerization procedure comprised placing 200 ml. of distilled water and the initiator in the bottle, which was then installed in the system. A rubber stopper was used as a closure for the glass reactor. A small glass cup was rigidly suspended from the stopper into the upper part of the reactor. Into this cup was placed any initiator or components thereof which might react before adjustment of the temperature and admission of the monomer. The reactor was deaerated by evacuation, monomer admitted to a pressure of 35–50 lb./sq. in. gage, reaction temperature attained, and shaking begun. At this point the initiator components and monomer were first brought together in solution where the polymerization took place. Polymerization conditions were maintained for ten minutes to two hours, or until approximately 2 g. of polymer was formed. The polymer always appeared initially as a colloidal dispersion which frequently coagulated partially or completely to white granules. When both forms of polymer existed at the end of a run, it was established that the radioactivity was the same in both fractions.

Isolation of Polymer and Radioactivity Assay.—Any colloidal polymer was coagulated either by freezing the dispersion or by adding saturated ammonium carbonate solution, and the polymer was isolated by filtration and washed thoroughly with distilled water and ethanol.

Radioactivity counts were made directly on the polymer with a Geiger counter. For this purpose, the best procedure found was to suspend the polymer in ethanol with violent agitation. This alcohol suspension was spread as uniformly as possible over the face of a circular micro cover glass 18 mm. in diameter and dried to constant weight at 100° . Sample thickness was such that there was 4 to 8 mg. per square centimeter. A control of benzidine sulfate prepared from the same radiosulfur and mounted like the polymer was counted alternately with the unknowns and the background. Sulfur content of the polymer was calculated from comparison with the control, thus eliminating the necessity for taking decay into consideration by calculation. Factors applied to correct for variations in sample size were determined by precipitation of known amounts of sulfur as benzidine sulfate with varying amounts of carrier to give precipitates in the weight range covered by the polymer samples. At least five samples of each polymer preparation were assayed and the mean of these determinations is reported. The mean deviation from the mean of all sulfur determinations was $\pm 4.8\%$ of the sulfur content of the polymers. It was established that the activity level of the sulfur employed was such that the radio assay method of analysis for sulfur was sensitive to less than 0.001% by weight.

Results and Discussion

The results are shown in Table I. Potassium

persulfate concentration was always 0.05% by weight in the reaction medium, and the concentration of sodium bisulfite, when used, was always 0.025%. Concentrations of any other adducts are given. Location of the radiosulfur is indicated by the asterisk.

In Experiment 1, the expectation, based upon investigations of other polymers,^{2,4,5} that sulfur-containing groups derived from the persulfate initiator would comprise at least some of the polymer end groups was not realized. In order to explore the possibility that sulfate end groups had been removed by hydrolysis, Experiment 2 was conducted at 0° and the polymer kept at 0° until it was isolated for counting. The precipitated iron powder was employed in the slightly acidified polymerization medium to provide a continuing source of ferrous ion as an oxidation–reduction promoter.⁶ Long period counts on the polymer were at the background level.

Two explanations of the observations that inactive polymers were obtained in Experiments 1 and 2 are possible: (1) sulfate ion-radicals^{5,7} initiate the polymerization and the resulting perfluoroalkyl sulfuric ester linkages are extremely rapidly hydrolyzed even at 0° , or (2) hydroxyl radicals from interaction of sulfate ion-radicals and water^{7,8} initiate the polymerization. In either event, it appears that persulfate-initiated polymer contains hydroxyl end groups at least in some stage of its history. The known instability to hydrolysis of this 1,1-difluorocarbonol structure⁹ suggests that the chain ends may ultimately be carboxyl groups.

Experiments 3 and 4 were identical except for the indicated location of the radiosulfur. It is to be noted that in this persulfate–bisulfite–iron oxidation–reduction initiator system, the polymer is inactive when the radiosulfur is in the persulfate and active when it is in the bisulfite. In order to make a rational interpretation of the relation between sulfur content and polymer molecular weight in Experiments 4, 5 and 6, it is necessary to know what initiating radicals are produced in the systems studied and the modes of chain termination.

(4) W. V. Smith and H. N. Campbell, *J. Chem. Phys.*, **15**, 338 (1947); H. Hopff, S. Goebel and R. Kern, *Makromol. Chem.*, **4**, 240 (1950).

(5) P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

(6) R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946).

(7) P. D. Bartlett and J. D. Cotman, Jr., *THIS JOURNAL*, **71**, 1419 (1949); D. Bunn, *Trans. Faraday Soc.*, **42**, 190 (1946); J. Y. MacDonald, *ibid.*, **42**, 193 (1946).

(8) M. G. Evans and J. H. Baxendale, *ibid.*, **42**, 196 (1946).

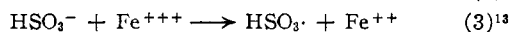
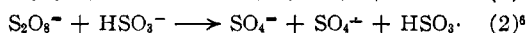
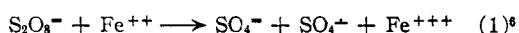
(9) F. Swarts, *Bull. soc. chim. Belg.*, **21**, 278 (1907); *Bull. soc. chim.*, **35**, 1534 (1924).

It is assumed in the case of tetrafluoroethylene polymerization initiated by inorganic free radicals that chain termination occurs by combination of a polymer radical with either another polymer radical or an initiator radical. In both cases there are only two end groups on each polymer molecule and each end group is derived from an initiator radical. Disproportionation and chain transfer with either polymer or monomer are improbable because of the great strength of the carbon-fluorine bond, which would have to be broken in either process.

Indications of the virtual absence of chain transfer in tetrafluoroethylene polymerization are believed evident in certain characteristics of the polymerization. When it is conducted in the presence of any one of a wide variety of organic compounds, telomers containing 1-25 tetrafluoroethylene units combined with one molecule of the chain transfer compound are obtained even at monomer pressures up to several hundred atmospheres.¹⁰ These telomers range from liquids to waxy solids which are completely lacking in toughness. On the other hand, when the polymerization is conducted in an aqueous medium with inorganic initiators, as reported herein, tough cold drawable polymers are obtained at temperatures at least as low as 0° and pressures near atmospheric. These observations indicate that the fluorocarbon radicals involved in tetrafluoroethylene polymerization are extremely reactive and that tetrafluoroethylene monomer and polymer are probably quite inert to chain transfer attack by these radicals.

In the free radical polymerization of ethylene, on the other hand, it is believed that chain transfer with polymer and monomer takes place.¹¹ This probably contributes to some extent to the difficulty in polymerizing ethylene to useful molecular weights. Ethylene requires about 1000 atmospheres pressure to yield polymers having DP's of only 450-800.¹²

In the persulfate-bisulfite-iron initiation system, the following pairwise interactions of all three components to produce free radicals appear to offer the most plausible account for the observations recorded in Table I.



Experiment 2 reveals that persulfate and Fe²⁺ react readily at temperatures as low as 0° yielding radicals which initiate tetrafluoroethylene polymerization to produce sulfur-free polymer. Reaction between persulfate and bisulfite was found in several experiments, including 5, to have an initiation threshold for tetrafluoroethylene at 35-36°. In Experiment 5, the system was buffered with borax to minimize the ionic concentration of any adventitious iron as well as certain other metals. Reaction between bisulfite and Fe³⁺

was found to have an initiation threshold at 0-10° for tetrafluoroethylene under our conditions.

It is apparent that in Experiment 4 reactions 1 and 3 probably effected the initiation and untagged end groups resulted from the former. The polymer molecular weight is, therefore, some unknown value less than 246,000. In Experiment 5 a similar situation exists in that some of the radicals and presumably end groups, are untagged. However, the two radicals are produced in equimolar proportions, and if they react equally readily with tetrafluoroethylene, the number average molecular weight is 267,000. Under these polymerization conditions of extremely low instantaneous monomer concentration as determined by the solubility and rate of solution of tetrafluoroethylene in the polymerization medium, it is possible that the sulfate ion-radical reacts further with bisulfite to produce the sulfonate radical or sulfite ion-radical from the bisulfite. In this event, the molecular weight is between 267,000 and 534,000.¹⁴

Polymer containing sulfur derived from bisulfite has been found to undergo no decrease in sulfur content when heated at 65° for three hours as a dispersion in water at pH 2-3. It has also been observed that dispersions of higher stability result from the use of bisulfite in the initiator. These observations are evidence that the ends of polymer molecules derived from bisulfite are probably sulfonate groups.

The result of Experiment 6 is probably not complicated by the participation of untagged free radicals. The polymer molecular weight is, therefore, very probably 142,000. In this experiment, the polymerization reaction was very short-lived because the initiation reaction went rapidly to completion. In view of this result and the profound effect of 2 p.p.m. of iron in the three-component initiator system, it appears, as reported by Wall and Swoboda for the benzoyl peroxide-sorbose oxidation-reduction initiation system¹⁵ that the iron functions as an electron carrier in an "oxidation-reduction cycle." The tetrafluoroethylene system is single phase, however, and initiator radicals are produced in both reactions of the iron. Qualitatively, reaction 1 appears to be the most rapid with 3 nearly as fast and 2 much the slowest as judged by their initiation threshold temperatures in tetrafluoroethylene polymerization. These reactions and their relative rates in tetrafluoroethylene initiation afford an explanation of the marked increases in initiation activity in going from persulfate to persulfate-bisulfite to persulfate-bisulfite-iron.

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(10) W. E. Hanford, U. S. Patents 2,411,158, 2,411,159, and 2,443,003.

(11) K. Nozaki, *Faraday Soc. Discussions*, "The Labile Molecule," No. 2, 337 (1947).

(12) R. B. Richards, *J. Inst. Pet.*, **34**, 237 (1948).

(13) C. F. Fryling, U. S. Patent 2,356,925.

(14) Commercial forms of "Teflon" tetrafluoroethylene resin are believed to have considerably higher molecular weights than those reported here because, although initiator concentrations are comparable, effective monomer concentrations in the polymerization medium are higher as a result of higher monomer pressure and more efficient agitation.

(15) F. T. Wall and T. J. Swoboda, *THIS JOURNAL*, **71**, 919 (1949).