

THE UNIVERSITY OF MICHIGAN
INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

THE EFFECTS OF GAMMA RADIATION
ON SEVERAL POLYSULFONE REACTIONS

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NOMENCLATURE

Latin Letters

C_H	Concentration of the hydrocarbon, $\frac{\text{gm mole}}{\text{liter}}$,
C_S	Concentration of the sulfur dioxide, $\frac{\text{gm mole}}{\text{liter}}$,
C_R	Concentration of the radicals, $\frac{\text{gm mole}}{\text{liter}}$,
d	Differential operator,
H	Hydrocarbon reactant
I	Radiation Intensity, $\frac{\text{kilorep}}{\text{hour}}$,
k	Reaction rate constant,
k_1, k_2, k_3	Constants defined in the text,
P, Q	Active hydrocarbon and sulfur dioxide radical reacting ends, respectively, of the polymerizing molecules,
R	Initiation rate function,
S	Sulfur dioxide reactant,
T	Temperature, °C,
T_C	Ceiling temperature, °C,
X	Dead, unreactive polymer,

Subscripts

i, f	Signify initial and final condition, respectively,
m, n	Signify molecular order corresponding to arbitrary molecular weights of the reacting molecules,
M	Exponential power,
p, d, t	Represent propagation, depropagation and termination processes,

Greek Letters

α	Constant, $\frac{k_{d,HS}}{k_{p,SH}}$,
β	Constant, $\frac{k_{d,SH}}{k_{p,HS}}$,
$[\eta]$	Intrinsic viscosity,
$\frac{\eta_{sp}}{c}$	Specific viscosity, concentration ratio
θ	Time,
Σ	Summation

THE EFFECTS OF GAMMA RADIATION ON SEVERAL POLYSULFONE
REACTIONS - PART I. PHYSICAL PROPERTIES OF THE COPOLYMERS

Introduction

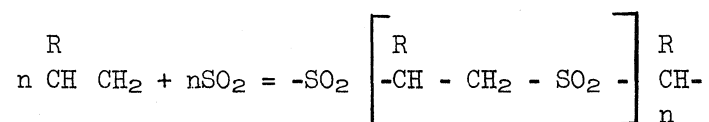
The advent of the atomic energy program stimulated many research activities to discover uses for the high-energy radiation made available in the fission products of the nuclear reactors. The use of this radiation as a catalyst in chemical reactions has been shown to be very effective in certain cases^(9,10) and may prove to be advantageous on an industrial scale.

In the absence of the fission-product sources and because of the expected use of gamma radiation, the experimental work at Michigan has been conducted with cobalt-60 sources nominally rated at 1 and 10 kilocuries. Actual intensity levels during the course of this investigation were about one-third the nominal values.

In the first part of this study, various hydrocarbons were reacted with sulfur dioxide under the influence of gamma radiation to produce copolymeric materials having many interesting physical properties. The second part of this study was concerned with the effect of radiation on the kinetics of the reactions.

The polysulfone reaction was first discovered by Solonina in 1898.⁽¹⁵⁾ He found that amorphous white compounds containing sulfur were produced by the addition of sulfur dioxide to allyl derivatives in benzene solution. These compounds were equimolar combinations of the sulfur dioxide and allyl reactants. Staudinger⁽¹⁶⁾ in 1932 postulated a linear, alternating polymeric structure for the ethylene-sulfur dioxide reaction.

Marvel and Weil⁽¹³⁾ showed that in all cases the copolymer had a "head-to-tail" structure based on the olefin reactant. The stoichiometric relation for the polysulfone reaction involving an olefin hydrocarbon was



where R represented some side chain group and n was a number corresponding to the molecular chain length.

The reaction proceeds under the influence of additive catalysts such as peroxides, nitrates, and other oxidizing agents,⁽¹⁴⁾ and it has been found that actinic light will catalyze the reaction⁽¹⁴⁾. Preliminary studies in this laboratory by Lewis⁽¹⁰⁾ showed that gamma radiation catalyzed the copolymerization of sulfur dioxide and ethylene. D'Emaus et. al.⁽⁶⁾ reported preliminary work on the reactions involving other olefins with sulfur dioxide under gamma radiation. Dainton, Ivin, and Sheard⁽⁵⁾ initiated a partial kinetics study of the copolymerization of 1-hexadecene and sulfur dioxide with beta particles from Sr-90 and Y-90.

A. REACTIONS STUDIED

The hydrocarbons which were reacted with sulfur dioxide in this study of the polysulfone reaction initiated by gamma radiation were:

- | | |
|--------------------------------|-----------------|
| 1. Ethylene | 6. n-Hexene-1 |
| 2. Propylene | 7. n-Decene-1 |
| 3. Butene-1 | 8. n-Dodecene-1 |
| 4. Butene-2 (cis
and trans) | 9. Cyclopropane |
| 5. Isobutylene | |

The reactions were carried out in the liquid phase under the vapor pressure of the reactant mixture. In all cases solid products were formed by the reactions in the gamma radiation field. Control runs made under similar conditions without radiation gave little or no product yield for any of the reactions.

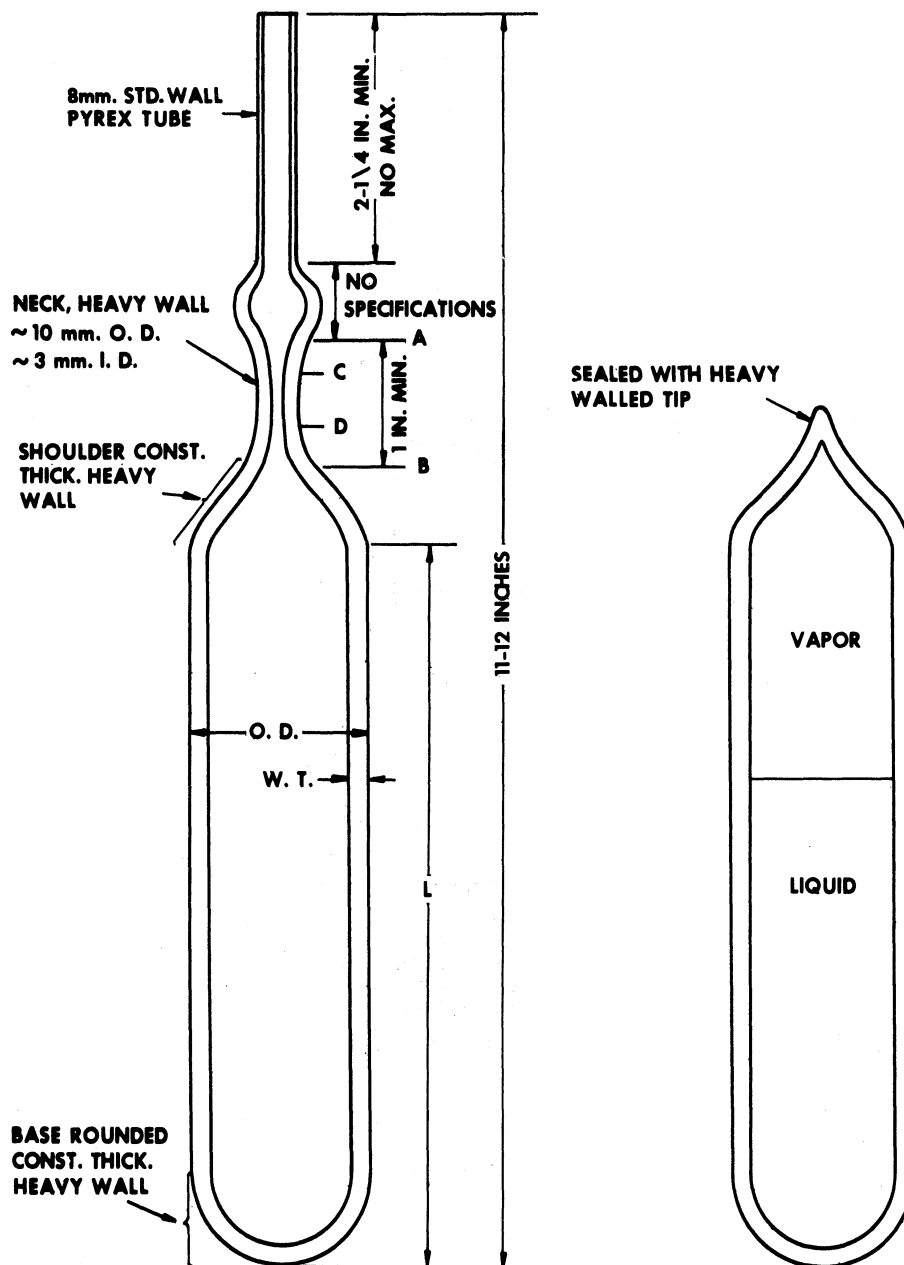


FIGURE 1. Drawing and Specifications for Pyrex Heavy Walled Glass Reactors.

<u>Reactor Designation</u>	<u>O. D. Inches</u>	<u>W. T. Inches</u>	<u>L. Inches</u>
A	$\frac{3}{4}$	$\frac{1}{8}$	$3\text{-}\frac{3}{4}$
B	$1\text{-}\frac{1}{2}$	$\frac{5}{32}$	$5\text{-}\frac{1}{2}$
C	1	$\frac{5}{32}$	6

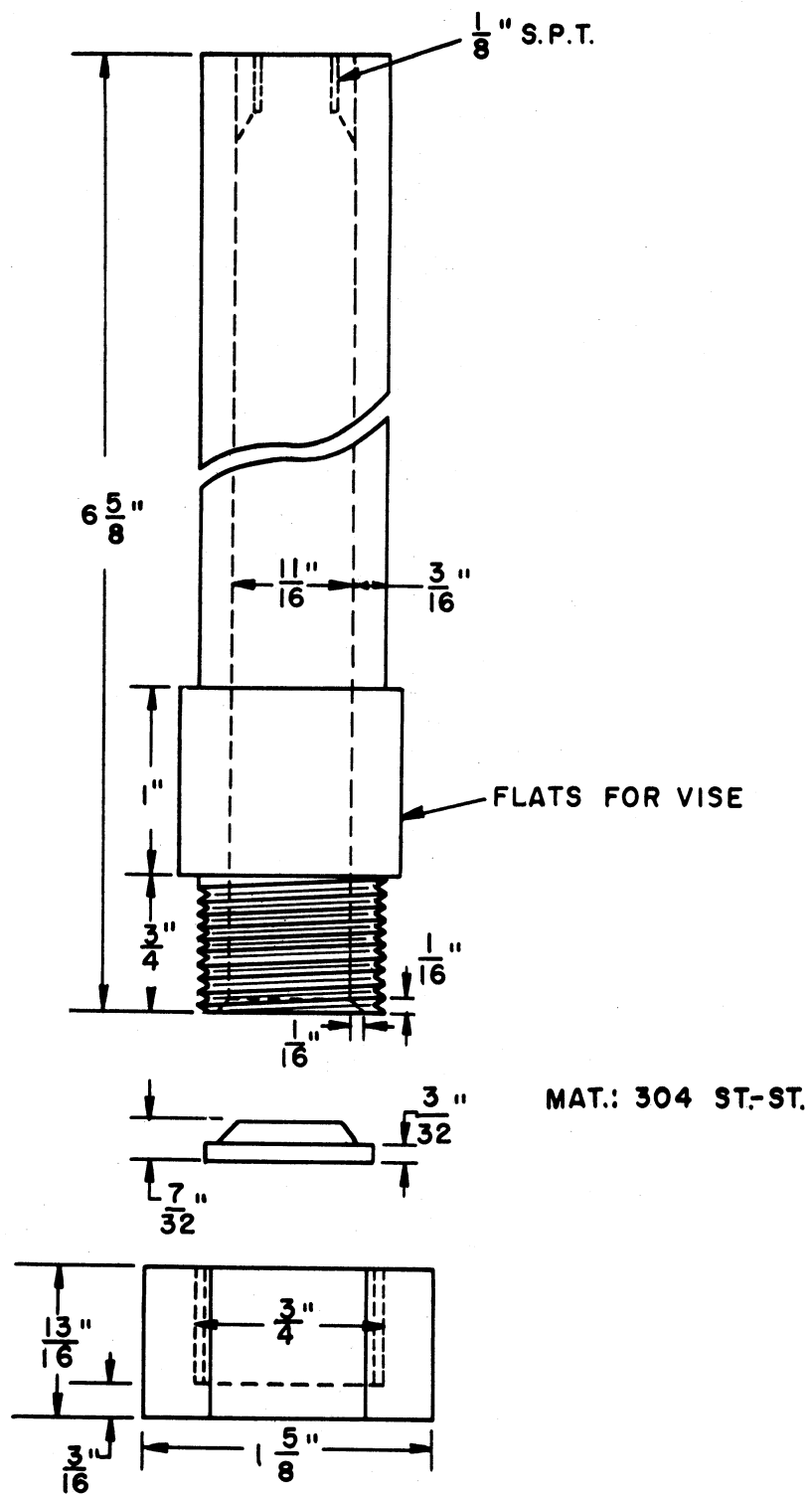


Figure 2. Working Drawing of the 30 Milliliter Stainless Steel Reactor No. D used for all Ethylene-Sulfur Dioxide Copolymerization Reactions.

B. EXPERIMENTAL WORK

1. Equipment Used.—All experimental data were taken using small batch reactors. The reactions of sulfur dioxide with all of the hydrocarbons except ethylene were carried out in reactors blown from heavy-walled, Pyrex tubing. Figure 1 is a drawing of these reactors before and after sealing. When sealed they would safely withstand pressures up to 300 pounds per square inch.

The reactions involving ethylene and sulfur dioxide were carried out in a 30 milliliter, stainless steel reactor. The reactor was provided with a tapered pressure seal under the closing cap and was capable of withstanding pressures up to 2000 pounds per square inch at 200° centigrade. A standard Hoke valve was attached to the reactor to facilitate loading and venting. A working drawing of the reactor is shown in Figure 2.

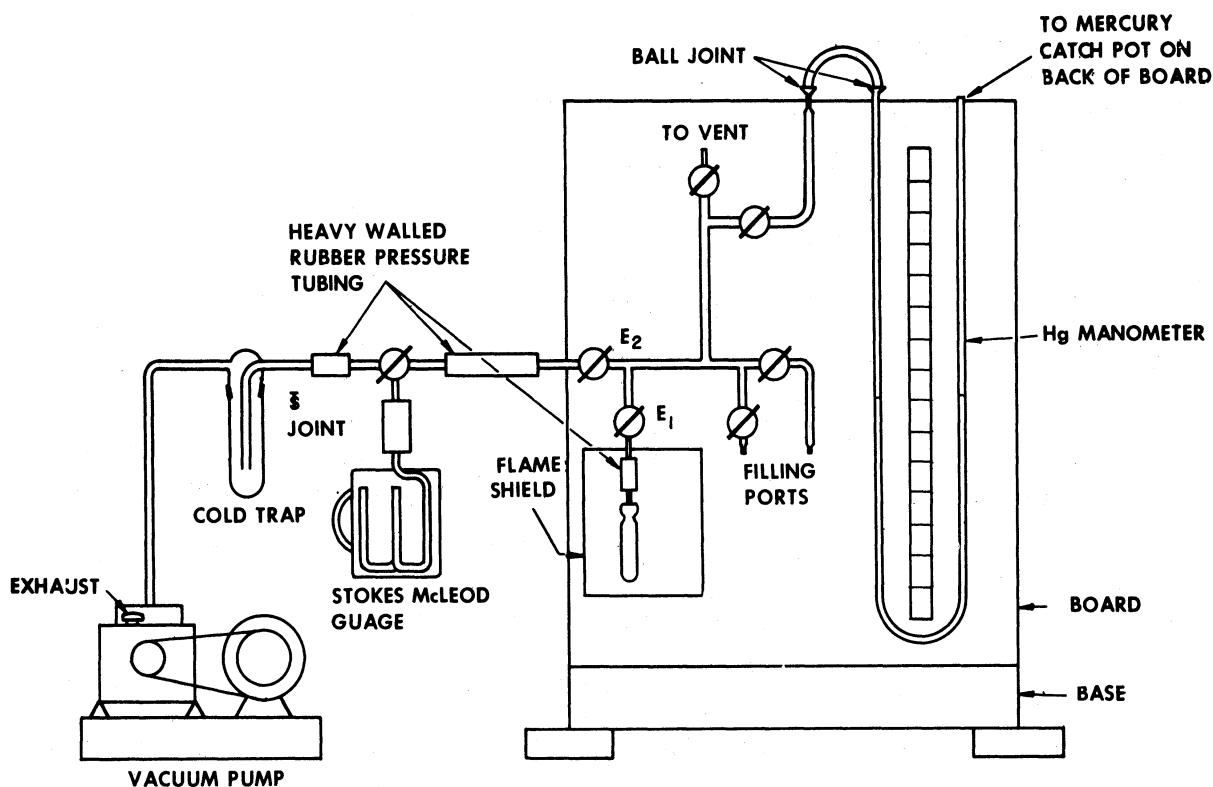


Figure 3. Schematic Diagram of the Reactor Loading Manifold.

Figure 3 is a schematic diagram of the gas loading rack constructed to facilitate loading the glass reactors. Heavy-walled Pyrex tubing and Pyrex vacuum stop cocks were used throughout, the rack was equipped with two filling ports and an emergency vent line to a hood. A mercury manometer was used to indicate loading and sealing pressure of the reactors. The evacuation system external to the rack consisted of a cold trap to condense vapors harmful to the pump, a McLeod gauge, and a standard Welch "Duo-seal" vacuum pump capable of producing less than 10 microns of Hg pressure. Dry ice in a 60-40% mixture of chloroform and carbon tetrachloride provided a temperature of -75°C for the condensing baths in both the cold trap and the cold bath around the vial. All connections to the rack were made with heavy walled rubber vacuum tubing sealed to the glass with Dekhotinsky cement.

A second, high pressure, stainless steel manifold was constructed to facilitate loading the stainless steel reactor in the ethylene, sulfur dioxide runs. This second manifold differed from the glass system by using standard Hoke 2000 psi valves and 6000 psi stainless steel tubing, and eliminating the manometer in the system.

2. Reactant Material Analysis.—The ethylene used in this work was a gift of the Dow Chemical Company. The other reactant materials were purchased from a variety of commercial suppliers. In general the materials were used directly as received, although in the case of the hexene-1, decene-1, and dodecene-1 further purification was deemed necessary. The hexene-1 was distilled on the laboratory Podbielniak distillation column at atmospheric pressure at a reflux ratio of 15:1 discarding the first and last quarter of each sample distilled. The n-decene-1 and n-dodecene-1 were distilled on the same column at a pressure of 20 mm Hg under the same external reflux conditions.

Analyses of all reactants except ethylene and sulfur dioxide were made on the laboratory Fisher-Gulf Partitioner, a commercial vapor phase chrom-

TABLE I. REACTANT MATERIAL ANALYSIS
 (Obtained by vapor-phase chromatography unless otherwise noted)

Reactant Material	Addit'l Treatment	Number Analysis Samples	Purity, Average Mole Percent	Impurities, Average Mole Percent			
				Oxygen	Acetylene	Ethane	
Ethylene O ₂ free	none	2	98.5	15 ppm	10 ppm	1.5	
Propylene C.P.	none	22	99.06	Propane 0.47	Butene-2 0.47	Butene-1 Trace	
Isobutylene C.P.	1. none 2. none	7 6	99.81 99.52	Butene-1 0.19	Butene-2 Trace	N-Butene Trace	Isobutane 0.12
Butene-2 C.P.	none	6	99.50	(22.30 cis (77.20 trans	0.15	Butene-1 0.21	
Butene-1 C.P.	1. none 2. none	4 10	99.73 99.57	Propylene 0.05	Butene-2 0.17	Isobutane 0.05	
N-Hexene-1 Batch 1.	one, atmos. Podbielniak Dist.L/D=15/1	7	99.50	0.11	0.24	0.08	
2.	Double	5	99.89	2-Methyl 0.50	Pentene-1		
3.	Pod. Dist. Pod. Dist.	3	99.89	0.11			
N-Decene-1	One, Red. Press. L/D=15/1	6	96.36	N-Decane (?) 0.38	N-Decene-2 (?) 3.64		
N-Dodecene-1	One, Red. Press. L/D=15/1	2	99.45	N-Dodecane or Meth. Subs. 0.55	Undecene (?)		
Cyclopropane C.P.	none	5	99.62	Ethylene (?) 0.11	Propane or Propylene (?) 0.15	N-Butane (?) 0.12	
Sulfur Dioxide (Anhydrous Grade)	none	Suppliers Analysis Spec.	99.988	Moisture 0.002	Non Condensables 0.010		

atography unit. Several duplicate analyses were made for each gas with good agreement in results. The average analyses determined for each reactant are presented in Table I. No attempt was made to analyze for trace amounts of inert gases. Several cubic feet of gas were vented from the top of the cylinders before use. The vial loading procedure was thought to eliminate most of the remaining, dissolved, non-condensable gases.

3. Loading Procedure.—A standard method for cleaning, loading, and irradiating the reactors was developed and followed in all cases. The reactors were cleaned by a series of caustic and acid washes, rinsed with distilled water and acetone, and dried in an oven for several hours.

The reactors were weighed before loading the reactants. Two loading methods were followed depending on the nature of the reactants used. Different procedures were necessary in loading a liquid and a gas to a reactor than were required if two gases were to be loaded.

In the case of the sulfur dioxide reaction with the liquid hydrocarbons (hexene, decene, or dodecene), the liquid was added to the reactor and the reactor was re-weighed. The reactor was connected to the loading rack of Figure 3 which had a cylinder of sulfur dioxide connected to one of the filling ports. The reactor was immersed in a cold bath until all bubbling and CO_2 evolution had ceased from the bath. The temperatures of the bath and hence of the reactor and its contents were then slightly less than -75°C . As a high vacuum was necessary to avoid possible inhibition of the reactions by the oxygen of the air, the whole system was evacuated to less than 1-mm Hg pressure. The sulfur dioxide was condensed in the reactor directly from the commercial cylinder.

When the desired amount of sulfur dioxide had been added, the system was evacuated to a pressure of 2 or 3 mm of Hg and the cold bath was lowered to permit heating by a natural gas-oxygen torch in the region AB on the reactor, as shown in Figure 1. After uniform heating of this region to a temperature close

to the softening point, the tip of the flame was concentrated on the region CD, which rapidly became soft. Due to the weight of the reactor, the region CD elongated and, since the external pressure was higher than the internal pressure, the wall collapsed upon itself, the end result being a fine tip capable of withstanding high pressure.

The sealed reactor was placed in the dark where it came to room temperature before reweighing to determine exactly the amount of sulfur dioxide added. It was then placed in a bath at the desired reaction temperature for several minutes before irradiation was started. The entire system was located in the radiation source field for a predetermined period of time while still at the desired temperature. The geometrical position with reference to the source determined the radiation intensity received.

After removal from the radiation field, the reactor was cooled to -75°C , broken at the tip and placed in a hood (in the dark) where the excess reactants escaped as the reactor came to room temperature. In cases where low vapor pressure hydrocarbon reactants were used and after the sulfur dioxide escaped in the hood, the reactors were placed in a vacuum desiccator jar connected to a cold trap and a vacuum pump. The excess hydrocarbon was removed under reduced pressure. The product was recovered, weighed, placed in the vacuum desiccator, evacuated, and reweighed periodically. When a constant weight was obtained, the product was bottled and stored for future analysis.

When two gaseous components were charged to a reactor, as was the case in the olefins of lower molecular weight, it was thought better to measure the amounts of condensed vapor by volume rather than by weight. The weighing procedure had two serious drawbacks: (1) the lines filled with air and, hence with oxygen, when the vial was disconnected from the system, and (2) the vial warmed up slightly during weighing and released sulfur dioxide and olefin vapors. The volumes were computed by comparison with a calibrated graduated vial and the

weights were obtained from densities found in standard reference handbooks. All other treatment was the same as described above.

4. Product Analysis Procedures. —Analysis procedures on the recovered product were, in general, made by well-known methods. In certain cases these methods were modified to fit a particular type of copolymer material. The physical properties that were investigated were melting or softening range, density, intrinsic viscosity, tensile strength, and elongation. The chemical properties investigated were sulfur content, solubility, and in certain cases, decomposition point.

Melting and softening ranges and decomposition points were measured by two methods. One method utilized a melting point bar of the design of Dennis⁽⁷⁾ and previously described in the literature.⁽¹⁰⁾ The second method utilized small capillary tubes in a Thiele tube containing a bath of Dow Corning Silicone D.C.550.

Densities were measured on finely divided copolymer products in calibrated picnometers using water for the fluid if the values were appreciably different from unity. If the density of the copolymer was near 1, measurements were difficult with water, and reagent ethanol or reagent butanol was then used as the fluid in the picnometer.

Intrinsic viscosities were determined in the normal manner using a modified Ostwald pipette in a constant temperature bath at $40.00 \pm .02^\circ\text{C}$.

Solubility was determined by weighing a small quantity of copolymer into known volume samples of various ordinary solvents. After standing several days with intermittent agitation, a sample of the liquid was taken and evaporated to dryness on a watch glass in the hood. No quantitative solubility tests were made, but qualitative observations were recorded.

For measurement of tensile strength and elongation of the copolymer, a film was molded in a standard hydraulic press at a temperature and pressure

dependent on the olefin material in the copolymer. From the molded film, tensile test specimens were cut with a standard die. The tensile strength and elongation were made on an Instron tensile tester at jaw speeds of one inch per minute.

Sulfur analyses were made in the laboratory by standard methods. The procedure followed was that outlined in Willard and Furman⁽¹⁸⁾ for the analysis of sulfur in vulcanized rubber. The exact procedure was reported by d'Emaus et. al.⁽⁶⁾

C. PRODUCT DESCRIPTION

After removal of the reactors from the radiation field and before opening them to recover the product, visual observations of the reacting masses were made. The appearances differed depending on the particular olefin reactant used. In several cases, noticeably the propylene, sulfur dioxide copolymer, there were some variations in appearance with the total dose received by the reacting solutions. The appearances were often different after molding into films. These observations are recorded below under subheadings according to the particular hydrocarbon reaction studied.

1. Ethylene-Sulfur Dioxide

Since the small stainless steel reactor No. D was used for these runs, no observations of the reacting masses were made. The copolymers were removed as white, opaque, finely divided powders which often could be shaken from the reactor. The copolymer could not be successfully molded at the pressures and temperatures that were available with the hydraulic press. Rather, a compressed mass was obtained which was opaque with a non-uniform greyish color. The discoloration indicated that some decomposition of the copolymer had taken place in the mold.

2. Propylene-Sulfur Dioxide

The reacting mixtures had varying degrees of clearness or opacity depending on the radiation dose received. The low dose copolymers were nearly clear. As the dose was increased, translucence and then opacity

appeared. The low dose copolymers were recovered as small crystals varying in size up to 1/4-inch in diameter. The medium dose copolymers caked in the reactors and had to be forceably removed while the high dose copolymers were often recovered as a finely divided, opaque powders. It was impossible to mold the copolymer into a continuous film. Rather, a hard sintered appearing sheet was obtained which was colored in various shades of brown. Two different molding conditions were tried. These were 3000 psi at 435°F and 3500 psi at 450°F.

3. Isobutylene-Sulfur Dioxide

The reacting mixtures contained finely divided copolymer particles dispersed throughout. On recovery, the copolymers remained finely divided and were poured from the reactors. Two attempts to mold the crude copolymers into continuous films were made. An attempt at molding the copolymer at 3000 psi at 460°F for 15 minutes resulted in its complete decomposition to a black powder. A second attempt with the copolymer was only slightly more successful. The molding conditions were 3000 psi at 355°F for 15 minutes. The center of the compressed mass was translucent film indicating some softening and flow. Around it, however, the film was very weak and crumbled to a powder on handling. A slight odor of SO₂ was detected during the molding operation indicating some decomposition of the copolymer.

4. Butene-1 Sulfur Dioxide

At low radiation doses, the copolymers apparently remained in solution as the reacting liquids did not have any visible characteristics different from the originally charged reaction mixtures. At medium and high doses, the copolymers sometimes formed in two layers in the reactors. The lower layer was a colorless, clear copolymer apparently dissolved in a sulfur dioxide rich phase while the upper layer was composed of white, opaque, solid particles apparently not soluble in the organic rich phase. The original reacting solutions at the temperature of the runs, however, were single phase liquids when charged to the reactors. The liquids apparently separated into two layers while standing in the

radiation field. On removal of the copolymers from the reactors, the white layers were tough chunks whereas the clear layers were plastic-like masses resembling polystyrene. These clear masses became hard and tough on standing, although still retaining their clearness. After a drying period to remove excess unreacted olefin and SO₂, sulfur analyses on the copolymers were made on several of the layers from different runs. These analyses showed the same sulfur composition in both layers. Melting point measurements indicated little because of the scatter of the data. In general, however, the observation was made that the clear copolymers softened sooner than the white opaque copolymers. Several of the copolymers were molded into colorless, transparent sheets under 3000 psi at 355°F for 15 minutes. The film from the press was hard, brittle, and clear. Tensile specimens were cut from the film with some difficulty and tensile strengths of the copolymer were measured. Both clear and white layer copolymers were used in molding the films as there was never enough of each to investigate the molding and tensile properties of the separate layers. Attempts to mold films at 410°F at 3000 psi were unsuccessful. The films were full of bubbles and sometimes appeared foamy. They were more brittle than those made at the lower molding temperature.

5. Butene-2-Sulfur Dioxide

The butene-2 copolymers were white, tough, hard masses and could only be removed from the reactors with some difficulty. The product from one run was in two layers similar to those described for some of the butene-1 copolymers. Here again the softening point of the clear copolymer was somewhat less than that of the white material. Clear, transparent, very brittle films were obtained from the molding operations at 3000 psi at 400°F for 15 minutes. The films sometimes cracked on cooling. No tensile test specimens could be cut from the films because of their extreme brittleness.

6. Hexene-1-Sulfur Dioxide

The low dose copolymers prepared from equimolar reactant solutions were, in general, white and opaque. Cloudiness appeared in the reactors after minutes of irradiation. This cloudiness gradually agglomerated to a white mass which, with further irradiation, became colorless and clear as the reaction proceeded to completion. The high dose copolymers remained colorless and clear when excess reactants were removed under vacuum. These transparent masses became hard and tough after the drying procedure. When an excess of sulfur dioxide was present in the reactors the reacting mixtures remained clear, but the viscosity of the mixtures increased markedly. This indicated that polymerization was taking place, but that the copolymers were soluble in the SO₂ rich reactants. After recovery from the reacting solutions, the copolymers were, in general, stringy white materials that clung together. When an excess of hexene was used, the cloudiness appeared as described above. The copolymers were apparently only slightly soluble in the excess hexene reactant.

In the runs where the hexene reactant was not purified, it was observed that some reaction took place before the reactors were put in the radiation field. The products from these reactors were in two solid phases like those described for the butene-1 copolymers. The clear, transparent layers turned pink after standing for several weeks in contact with the atmosphere.

The crude resins from the hexene-sulfur dioxide copolymers were relatively easy to mold. Colorless, transparent films were made which were more flexible than any of those described previously. The tensile specimens were punched from the films with a standard die without danger of cracking. Molding conditions were 3000 psi at 305°F for 15 minutes.

7. Decene-1-Sulfur Dioxide

The decene-sulfur dioxide copolymers remained in solution in the reacting mixtures. A viscosity increase of the reacting solutions was noticed as

the reactions went to completion. The recovered copolymers remained clear and colorless. They were rubbery immediately after removal from the reactors, but became tough after the vacuum drying process where excess reactants (generally decene monomer) were removed.

The copolymers molded easily at 3000 psi at 266°F. The film surfaces had a slightly "orange peel" appearance. Initially, the films were quite flexible, but after several weeks of exposure to the air they lost some of this flexibility.

8. Dodecene-1-Sulfur Dioxide

At 0°C, where the dodecene-sulfur dioxide reactions were made, the reactants formed two-phase liquids in reactors. As the reactions proceeded, however, the lower (SO₂) phase disappeared in all instances but one. In this case, single phase, colorless, clear products were formed which were soluble in the reactant mixtures. In one run, a two-layer solid product was recovered. Here, unlike the previously described examples where two-layer products were observed, the upper layer was clear and colorless while the lower layer was white and opaque. This indicated that the resulting copolymer was insoluble in sulfur dioxide and soluble in dodecene.

Colorless, clear films were molded from the run copolymer at 3000 psi and 230°F. The films were very flexible and could be creased without breaking. With prolonged exposure to the air at elevated temperatures the crude copolymers darkened through varying shades of brown.

D. EXPERIMENTAL RESULTS

The stoichiometric relation for the addition of sulfur dioxide to an olefin in the radiation initiated reaction was found to be the same as recorded in the literature for the peroxide initiated reaction. Sulfur analyses were made on many of the copolymers to confirm this relationship. With all of the hydrocarbon reactants studied except ethylene and cyclopropane, the sulfur analyses showed

that the products were truly copolymers containing equimolar amounts of sulfur dioxide and hydrocarbon.

The analyses on the ethylene sulfur dioxide copolymers indicated that the sulfur contents were lower than the equimolar values. Since Lewis⁽¹⁰⁾ has shown that ethylene will polymerize under gamma radiation, it may be possible that this reaction occurred in the reaction system.

Composition of the hexene-sulfur dioxide copolymer was not affected by temperature, intensity, or reactant concentration variation. All analyses showed a one-to-one mole ratio of sulfur dioxide to hexene in the product.

All sulfur analysis data are presented in Table II with the experimental reaction conditions. The calculated percentage sulfur based on equimolar addition appears in the "Remarks" column opposite the listing of hydrocarbon reactant used.

Melting or softening points and density measurements were made on most of the polysulfone reaction products. Tensile strength, elongation, and solution viscosity measurements were made on selected products from each of the reactions studied. The selection was made to include the whole range of radiation dose investigated and to indicate the overall effect of prolonged irradiation on the copolymers. The copolymer melting or softening ranges and densities appear in Table II. Tensile strengths, elongations, and intrinsic viscosity values are recorded in Table III.

The copolymer products from the reactions of sulfur dioxide with ethylene, propylene, isobutylene, and cyclopropane decomposed before any melting or softening occurred.

The low dose propylene--sulfur dioxide copolymers gave a slight indication of softening or melting just before the decomposition was noticed. This effect was not a distinct physical change and was not observed in the copolymers produced at longer reaction times. The radiation dose had very little effect

TABLE II. EXPERIMENTAL CONDITIONS FOR COPOLYMERIZATION OF VARIOUS HYDROCARBONS WITH SULFUR DIOXIDE

Run No.	Starting Date	Reactant Charge		Reaction Conditions		Irradiation		Irradiation		Product Recovered		Remarks
		Tot. Wgt. Gms	Hydro-carbon	gm. mol. SO ₂	ml. & React. Temp.	Temp. °C	Time hr.	Intensity kilorep/hr	Radiation dose kilorep	Wgt. gms.	Sulfur Analysis %	
1. Ethylene - Sulfur Dioxide												
Ethylene												
100	6-27-56	13.7	.146	.150	18.71	0	5.68	41.9	238	34.80	339-341D	1.74
101	7-10-56	14.88	.199	.145	22.85	0	2.03	41.9	85.1	26.68	323-325D	1.57
102	7-12-56	15.55	.203	.154	23.57	0	4.00	41.9	168	35.01	312-327D	1.69
103	7-13-56	15.97	.208	.158	24.19	0	8.03	41.9	336		339-359D	1.70
104	7-14-56	15.38	.135	.150	16.58	0	1.00	41.9	41.9	32.30	322-327D	1.99
105	7-16-56	15.95	.184	.164	23.25	0	1.00	41.9	21.0	27.52	325-327D	1.87
106	7-17-56	15.205	.164	.166	20.86	0	8.17	41.9	342	31.86	314-327D	1.67
107	7-18-56	15.690	.178	.167	22.08	0	5.75	41.9	241	29.169	314-324D	1.73
108	7-19-56	15.915	.149	.152	19.05	0	0.0	0.0	0.0		182-198D	
109	7-20-56	9.85	.351	0.0	28.89	0	8.40	41.9	352	.02	122-126	
Control-12.50hr-no rad.												
Isobutylene												
Isobutylene												
37	3-15-56	61.4	.542	.484	70.81	0	6.23	44.3	276	26.68	258D	1.33
39	3-15-56	64.2	.500	.565	70.54	0	19.55	44.3	857		247D	1.36
40	3-15-56	64.3	.530	.540	72.19	0	15.82	44.3	701	26.42	258D	1.38
41	3-15-56	66.1	.568	.543	74.92	0	11.90	44.3	527		255D	1.42
41C	3-15-56	73.0	.620	.595	82.95	0	0.0	0.0	0.0			
42	3-15-56	60.8	.505	.506	68.50	0	3.93	44.3	174	26.36	248D	1.40
50	4-2-56	42.78	.763	0	63.22	0 to 10	30.17	44.1	1330			
51	4-2-56	64.22	.538	.530	72.61	0	1.77	44.1	78.1		207D	1.63
52	4-2-56	55.54	.480	.443	65.41	0 to 10	15.00	44.1	662	24.06	258D	1.54
53	4-2-56	56.95	.492	.489	66.52	0 to 10	25.58	44.1	1120	24.45	253D	1.54
80	7-6-56	31.45	.560	0	50.89	0	90.13	42.3	3810			
86	7-26-56	54.55	.480	.432	62.79	0	10.00	42.0	420	.08	272D	1.57
92	7-26-56	55.62	.485	.443	63.84	0	16.00	42.0	672	21.34	253D	1.62
93	7-26-56	54.82	.467	.447	62.35	0	21.83	42.0	917	27.29	266D	1.44
94	7-26-56	55.04	.464	.452	62.36	0	27.00	42.0	1130	27.18	258D	1.57
98	8-3-56	62.35	.538	.502	72.69	0	2.00	41.8	83.6	25.72	262D	1.33
99	8-3-56	64.78	.525	.552	72.26	0	20.82	41.8	870	4.76	253D	1.49
Control-21.00hrs-no rad. couldn't recover product												
Bath warmed to 10°C overnight-couldn't rec. prod.												
Bath warmed to 10°C overnight												
Bath warmed to 10°C overnight												
Liquid product												

D denotes total decomposition
d denotes partial decomposition
C denotes clear polymer
W denotes white polymer

TABLE II (continued)

2. Propylene - Sulfur Dioxide

Run No.	Starting Date	Propylene MC-Day-Yr	Reactant Charge		Temp. °C	Reactant Conditions		Wgt. gms.	Product Recovered Sulfur Analysis %	Sulfur Softening Range °C	Density gm/ml.	Remarks
			Tot. Wgt. gms.	Gm. mol. hydro-carbon		Gm. mol. SO ₂	Irrad. Time hr.					
517	7-15-55		68	.88	.48	36.8	0	0	30.21	316d		Calc. for (C ₃ H ₆ SO ₂) _n Control 65.50 hrs no Rad.
518	7-18-55		79	.93	.62	104.7	26	2710.	29.44	283		
520	7-21-55		68	.76	.56	72.1	-75	2070.	29.23	273-316d		
521	7-26-55		65	1.55	0	130.0	27	2100.		148d		
528	8-11-55		82	1.19	.50	133.5	29	1080.	31.61	271-311d		
									29.80			
									28.75			
529	8-13-55		106	1.07	.95	134.9	25	462.	91.1	287d		
530	8-16-55		135	1.94	1.10	160.8	25	65.7	29.58	284		
533	8-16-55		128	1.18	1.23	186.9	27	32.3	29.02	167d		
534	8-17-55		223	2.23	1.97	286.5	27	180.	31.54	285d		
537	8-21-55		99	1.07	.84	129.9	28	1020.	29.06			
539	10-1-55		108.4	1.53	.69	157.3	19	399.	29.20			
540	10-7-55		116.8	1.08	1.12	143.0	25	375.	30.06			
541	10-12-55		151.5	1.41	1.42	162.6	20	719.	29.12			
542	10-19-55		126.5	1.13	1.23	148.8	17	541.				Oxygen admitted in loading
515	11-4-55		162.6	1.40	1.60	187.8	14	406.				
543	10-25-55		110.5	2.63	0	213.0	18	4690.				
									29.03			
27	2-23-56		57.0	.621	.498	68.93	0	497.	28.33	278-281d	1.46	
28	2-23-56		53.5	.596	.464	65.16	0	374.		258d	1.44	
29	2-23-56		58.1	.627	.492	70.48	0	274.		274-283d	1.38	
30	2-23-56		59.1	.564	.555	68.14	0	169.		271-278d	1.63	
31	2-23-56		58.4	.591	.509	69.45	0	56.1		274d	1.58	
31C	2-23-56		61.3	.629	.491	74.51	0	0		273-275		Control-22.00 hr-no Rad.
32	3-13-56		67.1	.602	.623	76.26	0	340.		272d	1.55	
33	3-13-56		62.0	.636	.601	72.13	0	723.		276-283d	1.49	
34	3-13-56		65.6	.614	.619	75.15	0	122.2	30.67	270-278d	1.50	
35	3-13-56		65.3	.621	.600	73.63	0	118.		270d	1.46	
36	3-13-56		68.6	.649	.641	79.01	0	559.	30.13	272d	1.50	
58	4-11-56		51.20	.551	.472	60.96	0	11.0	29.56	276-281d	1.48	
									29.18			
59	4-14-56		58.85	.512	.609	64.87	0	22.0	30.01	271-279d	1.43	
66	5-15-56		60.96	.599	.565	70.25	0	105.	32.50	272d	1.44	
67	5-15-56		57.67	.577	.537	67.34	0	45.5		275d	1.44	
68	5-16-56		60.36	.556	.583	68.55	0	4.33		274d	1.56	
									2.16			

TABLE II (continued)

3. Butene-2 - Sulfur Dioxide

Run No.	Starting Date Mo-Day-Yr	Reactant Charges		Temp. °C	Irrad. Time hr.	Reaction Conditions		Wgt. Gms.	Product Recovered Sulfur Analysis %	Density gm/ml.	Remarks	
		Tot. Wgt. Gms	Em. mol. SO ₂			Radiation Intensity kilorep/hr	Radiation dose kilorep					
Butene-2												
6	2-8-56	65.6	.610	.490	2.43	45.0	108.	37.97	26.68	1.52	Calc. for (C ₄ H ₈ SO ₂) _n	
7	2-8-56	60.0	.538	.465	1.01	45.0	45.5	15.80	25.17	1.33		
8	2-8-56	64.8	.633	.457	.51	45.0	23.0	7.49	25.97	1.67	possible product loss	
9	2-8-56	60.1	.577	.433	.26	45.0	11.7	1.26		1.55	possible product loss	
10	2-8-56	55.6	.538	.396	.08	45.0	3.60	.35			possible product loss	
10C	2-8-56	56.9	.547	.411	0	45.0	0	.03			Control-2.85 hrs. no rad.	
8A	2-8-56	59.8	.584	.423	0	45.0	23.0	6.39				
9A	2-8-56	57.5	.487	.470	.26	45.0	11.7	1.90				
10A	2-8-56	57.9	.492	.470	.08	45.0	3.60	1.47				
11	2-14-56	59.1	.530	.458	0	45.0	391.	40.68				
12	2-14-56	59.4	.505	.456	0	45.0	303.	41.22	26.68	1.52	Temp. increase to 7°C	
13	2-14-56	57.4	.502	.456	0	45.0	253.	41.50		1.40	Temp. increase to 4°C	
14	2-14-56	58.5	.533	.447	0	45.0	210.	38.41		1.58	Temp. increase to 2°C	
15	2-14-56	62.2	.570	.472	0	45.0	167.	38.90		1.55		
25	2-18-56	5.8	.103	0	0	45.0	0	0		1.49		
26	2-18-56	6.8	.118	0	0	44.9	0	0			Control-72.83 hrs no rad.	
72	6-19-56	58.56	.528	.452	2.95	42.8	126.	36.03	24.81	1.62		
73	6-19-56	59.76	.545	.454	1.58	42.8	67.6	27.43	24.99	1.58		
95	8-7-56	63.25	.519	.553	9.07	41.7	378.	51.36		1.51		
96	8-7-56	69.78	.615	.550	4.00	41.7	167.	47.90		1.50	2 prod. layers C223-238	

TABLE II (continued)

4. Butene-1 - Sulfur Dioxide

Run No.	Starting Date	Mo-Day-Yr	Reactant Charge		Temp. °C	Reaction Conditions		Wgt. gms.	Sulfur Analysis %	Product Recovered Range °C	Density gm/ml.	Remarks
			Tot. Wgt. gms	Hydro-carbon		Irrad. Time hr.	Intensity kilorep/hr					
Butene-1												
1	2-7-56		61.2	.531	0	7.53	45.0	339	21.7	203-240	1.58	Calc. for (C ₄ H ₈ S ₂) _n
2	2-7-56		63.7	.524	0	5.75	45.0	259	11.44	190-240	1.42	
3	2-7-56		60.7	.529	0	3.82	45.0	172	5.31	160-238	1.54	
4	2-7-56		61.7	.512	0	2.10	45.0	94.5	.89	166-246		
5	2-7-56		57.4	.481	0	1.15	45.0	51.8	.49	223-239		
5C	2-7-56		55.2	.461	0	0	0	0	<.05			
16	2-17-56		62.2	.577	0	9.43	44.9	423	45.58	212-236	1.44	Control-19.50 hrs-no rad Not able to recover product
17	2-17-56		59.7	.487	0	11.43	44.9	513	46.02	C222-233 W231-239	1.45	
18	2-17-56		65.1	.586	0	13.93	44.9	625	45.87	222-236	1.48	2 prod. layers
19	2-17-56		62.2	.594	0	16.77	44.9	753	46.30	C233-243 W228-241	1.42	
20	2-17-56		59.3	.567	0	21.97	44.9	986	43.80	C255-241 W221-235	1.50	2 prod. layers
21	2-18-56		5.0	.089	0	0	0	0	0			
22	2-18-56		7.0	.125	0	25.42	44.9	1140	0			
69	8-18-56		55.70	.463	0	11.88	42.8	508	45.02	224-248	1.60	2 prod. layers
70	8-18-56		58.86	.492	0	10.05	42.8	430	44.58	217-246	1.58	
71	8-18-56		56.74	.464	0	8.12	42.8	348	22.22	C223-243 W235-246	1.49	
97	8-9-56		62.18	.504	0	23.62	41.7	985	56.17	175-235		
150	9-10-56		62.29	.515	0	15.70	41.1	645	55.69		1.24	2 prod. layers
151	9-10-56		67.51	.568	0	20.50	41.1	843	60.54		1.29	
132	9-10-56		67.80	.568	0	12.50	41.1	514	57.76		1.28	2 prod. layers
133	9-13-56		64.03	.517	0	10.00	41.1	411	54.07		1.43	
134	9-13-56		66.19	.563	0	7.00	41.1	288	49.00	C223-233 W228-242	1.36	1 in. OD reactor in lg. bath
137	10-3-56		21.47	.184	0	1.22	41.1	50.1	.43	217-230		
138	10-3-56		24.77	.204	0	2.40	62.7	150	1.30	208-228		
139	10-4-56		19.70	.156	0	1.00	62.7	82.7	.49	208-228		
140	10-4-56		21.20	.174	0	1.50	62.7	31.4	.08	218-227		
141	10-4-56		22.53	.199	0	1.00	62.7	62.7	.05	213-225		
142	10-4-56		20.53	.184	0	3.10	62.7	194	2.02	233-238		
143	10-4-56		21.93	.182	0	5.42	62.7	340	5.64	238-244		

TABLE II (continued)
5. Hexene-1 - Sulfur Dioxide

Run No.	Starting Date	Reactant Charge		Temp. Irrad.	Reaction Conditions	Wgt. Gms.	Product Recovered	Density	Remarks
Hexene-3	Mo-Day-Yr	Tot. Gms	Gm. mol. SO ₂	Time hr.	Intensity KIlorep/hr	ml. at react. temp.	Sulfur Sotening Range °C	Gm./ml.	
54	4-12-56	53.36	.359	0	44.0	59.80	172-213	1.19	Calc. for (C ₆ H ₁₀ SO) ₂ Pod. Dist Hexene ² rdns 54.55.78 Control-4.33 hrs. no rad.
55	4-12-56	55.17	.374	0	0	61.99	172-198		
75	7-2-56	32.28	.584	0	65.6	46.65	W215-221		(Runs 81 to 85, 110, Hexene not distilled before run. (Apprec. react. to start. (All had 2 phase product. (Turned pink on standing
81	7-3-56	53.21	.374	0	65.6	60.61	W216-219	1.16	
82	7-3-56	54.29	.371	0	65.6	61.21	W208-214	1.32	
83	7-3-56	56.23	.370	0	65.6	62.49	W201-215		
84	7-3-56	53.90	.366	0	65.6	60.38	W194-203	1.46	
85	7-10-56	46.29	.377	0	0	55.98	W218-225		
110	8-8-56	24.56	.169	0	64.4	27.76	W198-221		
111	8-9-56	22.43	.143	0	0	24.61	W219-227		
112	8-10-56	25.23	.180	0	64.4	28.90	W198-221		
113	8-14-56	23.88	.165	0	41.6	27.02	W198-221		
114	8-14-56	22.81	.153	0	41.6	25.59	W198-221		
115	8-14-56	23.79	.156	0	41.6	26.92	198-214	1.17	
116	8-14-56	26.60	.171	0	41.6	29.30	198-213	1.02	
117	8-14-56	22.45	.154	0	41.6	25.37	198-218		
118	8-14-56	24.00	.148	0	64.1	26.37	198-218		
119	8-16-56	25.88	.162	0	64.1	28.30	200-214	1.13	
120	8-16-56	26.81	.183	0	64.1	30.19	198-208	1.20	
121	8-16-56	26.07	.174	0	64.1	28.15	208-221	1.11	
122	8-31-56	26.53	.183	0	63.9	28.99	196-208		
200	10-18-56	20.20	.141	0	62.2	20.60	167-198		Control 5.00 hr. no rad. Pod. Dist. All Hexene for runs from here on, distilled on Podbielniak Column.
201	10-18-56	19.01	.126	-77.3	62.2	20.42	198-223	1.06	60-40 CHCl ₃ -CCl ₄ slush bath, 2 phase liq. reactant
202	10-18-56	19.81	.121	-23.3	62.2	20.99	220-223		MgCl ₂ slush bath, 14. reactant
203	10-18-56	20.13	.130	-14.0	62.2	21.47	203-223		MgCl ₂ slush bath, 2 phase prod
204	10-18-56	20.49	.124	-24.0	62.2	22.09	213-218		MgCl ₂ slush bath, 2 ph. pro
205	10-18-56	21.32	.130	0	62.2	23.88	218-228	1.14	Ice bath
206	11-15-56	19.56	.124	+23.0	61.0	22.28	182-205	1.12	Water bath
207	11-15-56	19.75	.132	+23.6	61.0	23.80	203-221	1.15	Water bath
208	11-15-56	21.43	.139	+46.3	61.0	25.03	203-227	1.09	Water bath
209	1-24-57	18.72	.121	+35.2	58.8	20.95	192-233		Water bath
210	1-24-57	19.13	.125	+9.1	58.8	22.24	203-241		Water bath
300	10-16-56	21.43	.150	0	62.2	24.35	204-217	1.18	
301	10-16-56	18.55	.0883	0	62.2	18.57	219-231	1.21	
302	10-16-56	19.10	.0811	0	62.2	18.53	W217-229	1.19	
303	10-16-56	20.39	.128	0	62.2	22.27	W210-232	1.20	

TABLE II (continued)

5. Hexene-1 - Sulfur Dioxide

Run No.	Starting Date Mo-Day-Yr	Reactant Charge		Tot. Vol. ml. at react. temp.	Temp. °C	Time hr.	Reaction Conditions		Wgt. Gms. Sulfur	Product Recovered	Density gm/ml.	Remarks
		Hydro-Carbon	SO ₂				Intensity kilorep/hr	Radiation dose kilorep				
304	10-16-56	16.69	.145	20.79	0	0.750	62.2	46.7	2.64	21.02	205-250	1.20
305	10-16-56	15.90	.142	18.65	0	0.750	62.2	46.7	2.66	21.05	211-229	1.21
306	11-14-56	18.88	.0500	16.31	0	0.750	61.0	45.8	2.33		198-217	1.14
307	1-24-57	12.71	.0442	11.65	0	0.750	59.8	44.1	2.56		210-245	
308	1-24-57	15.54	.122	18.53	0	0.750	58.8	44.1	3.47		200-240	
309	1-24-57	16.45	.156	21.41	0	0.750	58.8	44.1	5.97		210-244	
310	1-24-57	20.83	.0490	17.60	0	0.750	58.8	44.1	2.94		215-246	
311	2-16-57	14.01	.126	17.68	0	0.750	58.0	43.5	5.96		197-228	1.22
312	2-16-57	14.74	.123	18.04	0	0.750	58.0	43.5	4.77		192-225	1.22
313	2-16-57	20.41	.0747	18.94	0	0.750	58.0	43.5	2.91		203-223	1.17
314	2-16-57	17.09	.116	19.22	0	0.750	58.0	43.5	2.72		197-233	1.10
315	2-16-57	13.44	.128	17.42	0	0.750	58.0	43.5	3.66		192-228	1.22
316	2-16-57	13.08	.129	17.26	0	0.750	58.0	43.5	4.14		192-228	1.21
317	2-16-57	17.88	.169	23.07	0	0.750	58.0	43.5	6.06		203-230	1.22
318	3-26-57	16.99	.117	19.21	0	0	0	0	.15		172-193	
319	3-26-57	14.35	.112	17.07	0	.200	57.0	11.4	.28		172-193	Control-5.53 hrs. no rad.
320	3-27-57	13.46	.116	16.70	0	.367	57.0	20.9	.58		198-233	Runs 518-327-Phillips Res. Grade Hexene 99.64/ pure Stored over Sodium for 2 months
321	3-27-57	12.32	.115	15.82	0	.367	57.0	20.9	.71		203-233	
322	3-27-57	11.36	.114	15.13	0	.367	57.0	20.9	.49		203-233	
323	3-27-57	11.16	.117	15.17	0	.367	57.0	20.9	.81		198-235	
324	3-27-57	13.07	.121	16.76	0	.200	57.0	11.4	.23		203-233	
325	3-27-57	12.02	.121	15.98	0	.200	57.0	11.4	.19		203-233	
326	3-27-57	14.43	.117	17.45	0	.200	57.0	11.4	.33		203-233	
327	3-27-57	19.10	.0681	17.60	0	.200	57.0	11.4	.65		203-237	
400	10-25-56	19.11	.125	21.17	0	0	0	0	.31		162-182	Control-5.50 hrs. no rad.
401	10-25-56	20.36	.139	22.96	0	0.0583	987	57.5	2.37	21.17	188-213	Pneonix Center Well
402	10-25-56	19.27	.136	22.02	0	0.0708	987	69.9	2.23		193-228	Pneonix Center Well
403	10-25-56	19.46	.141	22.46	0	0.125	383	47.9	1.75		187-230	Pneonix tangent outside
404	10-25-56	19.13	.134	21.78	0	0.142	383	54.4	2.81		182-233	Pneonix tangent outside
405	10-30-56	19.94	.135	22.34	0	0.283	156	44.2	2.20		193-230	F.P.L. CW.
406	10-30-56	21.91	.164	23.80	0	0.350	156	54.6	4.61		208-228	F.P.L. CW.
407	11-13-56	19.58	.127	21.66	0	17.72	3.58	63.4	7.25	22.10	197-215	1.19
408	11-13-56	19.48	.132	21.90	0	17.72	3.58	63.4	7.41		W201-220 C183-218	1.18
409	11-14-56	19.67	.123	21.49	0	0.750	62.5	46.9	3.29		203-223	1.21
410	1-15-57	20.40	.133	22.57	0	2.33	23.0	4.84	4.64		209-227	1.14
411	1-24-57	19.61	.131	21.69	0	0.283	151	42.7	3.32		182-235	F.P.L. C.W.
412	1-24-57	21.56	.134	23.44	0	0.300	151	45.5	5.70		182-238	F.P.L. C.W.

TABLE II (concluded)

		6. n-Decene-1 - Sulfur Dioxide				n-Dodecene-1 - Sulfur Dioxide				Cyclopropane - Sulfur Dioxide					
Run No.	Starting Date Mo-Day-Yr	Reactant Charged		Temp. °C	Irrad. Time hr.	Reaction Conditions		Wgt. gms. Sulfur Analysis %	Product Recovered Sulfur Softening Range °C	Density gm/ml.	Remarks				
		Tot. Wgt. Gms	Hydro-carbon			mol. S ₂	mol. SO ₂					Intensity kilorep/hr	Radiation dose kilorep		
56	4-12-56	48.87	0.242	.231	0	55.13	0	3.50	44.0	154	184	15.61	160-195	1.05	Calc. for (C ₁₀ H ₂₀ SO ₂) _n
57	4-26-56	46.65	0.227	.231	0	52.47	0	0	0	0	0	15.26	160-195	1.05	Control-3.17 hr no rad. Small amt. liquid product
60	4-26-56	46.19	0.217	.245	0	51.28	0	.62	43.8	27.2	27.2	15.01	160-205	1.06	
61	4-26-56	52.11	0.226	.230	0	56.12	0	1.33	43.8	58.3	58.3	15.30	180-215	1.06	
62	4-26-56	47.76	0.208	.231	0	51.54	0	1.25	43.8	11.0	11.0	4.74	162-198	1.06	
63	4-26-56	46.66	0.219	.250	0	51.78	0	.08	43.8	3.50	3.50	2.28	160-185	1.06	
64	5-15-56	40.76	0.220	.155	0	47.72	0	2.17	43.3	94.0	94.0	36.87	160-185	1.06	
77	6-20-56	31.00	0.221	0	0	41.01	0	1.16	42.8	4970.	4970.	19.05	170-210	1.06	
129	8-31-56	20.60	0.101	.100	0	23.24	0	2.00	63.8	128.	128.	13.80	182-212	1.06	Calc. for (C ₁₂ H ₂₄ SO ₂) _n 2 phase liq. reactants for all Dod. runs
76	6-20-56	43.05	0.188	.177	0	48.87	0	1.85	42.7	79.0	79.0	12.79	104-138	1.06	Dodecene not distilled some decomp. on evac.
79	7-2-56	33.54	.199	0	0	43.33	0	90.52	42.4	3840.	3840.	13.95	150-161	1.015	" " " " " "
87	7-10-56	50.00	.214	.219	0	56.25	0	.62	42.2	26.2	26.2	4.39	143-177	1.012	" " " " " "
88	7-10-56	46.06	.201	.191	0	52.22	0	1.37	42.2	57.8	57.8	14.05	159-176	1.06	Control 5.00hr no rad. Dod.
89	7-10-56	47.86	.203	.215	0	52.66	0	1.75	42.2	73.9	73.9	1.10	163	1.06	2 phase product
90	7-10-56	51.88	.222	.228	0	58.36	0	0	0	0	0	12.43	182-207	1.23	2 phase product
123	8-22-56	23.87	.087	.143	0	25.40	0	2.10	63.8	134.	134.	1.45	132-208	1.017	2 phase product
124	8-21-56	24.62	.087	.156	0	25.86	0	0	0	0	0	26.50	153-161	1.017	2 phase product
125	8-21-56	22.23	.089	.112	0	24.46	0	1.22	63.8	77.8	77.8	13.95	118d-140D	1.06	Control 4.66hr no rad.
126	8-22-56	19.91	.088	.080	0	22.68	0	.52	63.8	33.2	33.2	1.15	128d-142D	1.06	
127	8-22-56	21.76	.085	.118	0	23.63	0	.25	63.7	16.0	16.0	1.45	132d-142D	1.06	
128	8-31-56	22.70	.085	.131	0	24.34	0	1.10	63.7	6.37	6.37	26.50	153-161	1.017	
135	9-18-56	30.07	.119	.157	0	32.88	0	2.75	63.1	174.	174.	15.11	118d	1.06	Calc. for (C ₃ H ₆ SO ₂) _n
136	9-18-56	27.88	.112	.139	0	30.72	0	.65	63.1	52.4	52.4	30.21	118d	1.06	
43	3-27-56	57.8	.698	.444	0	66.21	0	42.28	44.1	1870	1870	.15	118d-140D	1.06	
44	3-27-56	50.0	.697	.479	0	67.70	0	58.40	44.1	2580	2580	.18	118d-140D	1.06	
45	3-27-56	59.2	.675	.481	0	66.35	0	33.97	44.1	1500	1500	.11	118d-140D	1.06	
46	3-28-56	61.3	.685	.507	0	68.16	0	24.58	44.1	1080	1080	.11	118d-140D	1.06	
47	3-28-56	64.6	.709	.543	0	71.35	0	10.63	44.1	469	469	.07	118d-140D	1.06	
47C	3-27-56	64.0	.707	.535	0	70.88	0	0	0	0	0	.00	118d-140D	1.06	
48	4-2-56	59.28	.682	.478	0	66.66	0	4.52	44.1	199	199	.05	118d-140D	1.06	Control-44.58 hr. no rad.
49	4-2-56	41.10	.954	0	0 to 10	63.35	0	31.95	44.1	1410	1410	.00	118d-140D	1.06	Bath warmed to 10°C overnight
75	6-19-56	55.81	.583	.489	0	60.54	0	138.43	42.8	5930	5930	.32	118d-140D	1.06	

TABLE III. PHYSICAL PROPERTIES AND MOLECULAR WEIGHT ESTIMATION OF SOME POLYSULFONE RESINS PRODUCED BY GAMMA RADIATION

Run No.	Hydrocarbon Reactant	Reaction Conditions				Tensile Strength psi	Elongation inches/inch	[η] deciliters/gram	Remarks
		Initial Composition molesH/moles	Irrad. time hrs.	Radiation Intensity Krep/hr.	Radiation Dose kilorep				
103	Ethylene	1.32	8.03	41.9	336.	-	-	Molding attempt	
104	Ethylene	.895	1.00	41.9	41.9	-	-	Not soluble	
106	Ethylene	.988	8.17	41.9	342	-	-	Not soluble	
28	Propylene	1.29	8.53	44.9	374	-	-	Molding attempt 455°F@3000psi	
32	Propylene	.960	7.66	44.4	340	-	-	Molding attempt 450°F@3000psi	
36	Propylene	1.01	12.58	44.4	559	-	-	Not soluble	
67	Propylene	1.08	1.05	43.3	45.5	-	-	Not soluble	
20	Butene-1	1.32	21.97	44.9	986	5,210	.087	AVG. of 2 samples	
70	Butene-1	1.01	10.05	42.8	430	6,770	.096	AVG. of 3 samples	
134	Butene-1	1.04	7.00	41.1	288	7,700	.077	AVG. of 3 samples	
97	Butene-1	.952	23.62	41.7	985	-	.123 P	Film molded-too brittle for T.S.	
143	Butene-1	.992	5.42	42.7	340	-	.146 P	Film molded-too brittle for T.S.	
6	Butene-2	1.24	2.43	45.0	109	-	.150 P	Film molded-too brittle for T.S.	
7	Butene-2	1.16	1.01	45.0	45.5	-	-	Film molded-too brittle for T.S.	
12	Butene-2	1.04	6.73	45.0	303.	-	-	Film molded-too brittle for T.S.	
11	Butene-2	1.16	8.68	45.0	391.	-	.140 P	cracked on cooling	
37	Isobutylene	1.12	6.23	44.3	276	-	-	Molding attempt complete decomposition	
92	Isobutylene	1.09	16.00	42.0	672	-	-	Molding attempt	
94	Isobutylene	1.02	27.00	42.0	1130	-	-	Not soluble	
98	Isobutylene	1.07	2.00	41.8	83.6	-	-	Not soluble	
54	Hexene-1	1.00	3.50	44.0	154	3,095	.039	AVG. of 3 samples	
82	Hexene-1	1.03	2.25	65.6	147	3,131	.051	AVG. of 5 samples	
120	Hexene-1	1.02	.98	64.1	62.8	2,953	.032	AVG. of 3 samples	
116	Hexene-1	.898	.50	41.6	20.8	-	2.00 T		
113	Hexene-1	1.05	4.53	41.6	188.	-	1.30 T		
407	Hexene-1	.920	17.72	3.58	63.4	-	.166 P		
401	Hexene-1	1.03	.0583	987.	57.5	-	.125 P		
200	Hexene-1	1.08	.750	62.2	46.7	-	.325 P		
60	Decene-1	.890	.62	43.8	27.2	1,602	.070	AVG. of 6 samples	
61	Decene-1	1.03	1.33	43.8	58.3	380	.022	AVG. of 4 samples, poor film to start	
129	Decene-1	1.01	2.00	63.8	128.	1,680	.044	AVG. of 2 samples.	
62	Decene-1	.720	.25	43.8	11.0	-	3.0 T		
89	Dodecene-1	.946	1.75	42.2	75.9	1,430	.098	AVG. of 4 samples	
126	Dodecene-1	1.10	.52	63.8	33.2	1,122	.046	AVG. of 3 samples	
135	Dodecene-1	.760	2.75	63.1	174.	1,491	.086	AVG. of 5 samples	
127	Dodecene-1	.718	.25	63.8	16.0	-	4.1 T		
76	Dodecene-1	1.06	1.85	42.7	79.0	-	-	Could not be dissolved-Fibrous clear polymer remained.	

P denotes Pyridine for viscosity measurement
T denotes Tetraline for viscosity measurement

on the decomposition points.

The butene-1, butene-2, hexene-1, decene-1, and dodecene-1 polysulfones had fairly distinct softening or melting ranges without decomposition. The butene-1 and butene-2 copolymer melting and softening ranges remained relatively constant over the entire range of reaction time. The actual temperatures increased slightly with reaction at low times. At the longer reaction times, the temperature remained relatively constant.

In the case of the decene-1-sulfur dioxide copolymers there was no effect of the time of reaction on the temperature where melting started. The temperature at which the melting was completed increased at low reaction times to a maximum at about 1.25 hours. This temperature decreased steadily over the high reaction times. In the case of the dodecene-1-sulfur dioxide copolymers, both the initial and final melting temperatures went through minimums in the range of reaction times studied. The high dose dodecene copolymers were sometimes discolored when they were completely melted.

The effects of reaction time, radiation intensity, reaction temperature, and reactant composition on the melting range of n-hexene-1-sulfur dioxide copolymers are found in Figure 4. As shown in Figure 4a, both initial and final melting temperatures increased with low reaction times through maximum values at about 0.75 hours before decreasing with high reaction times. The hexene-1 copolymer softening and melting temperatures increased through similar maximum values as functions of the radiation intensity as is shown in Figure 4b. Figure 4c shows the melting points of the copolymers were a function of the reaction temperatures of the lower temperatures. The melting points were independent of reaction temperatures above -20°C . At the lower temperatures, the reaction systems were two-phase liquids which could have an effect on the molecular composition of the copolymers if the reactions occurred at this liquid-liquid interface. The ratio of concentration of the hexene to the sulfur dioxide monomers

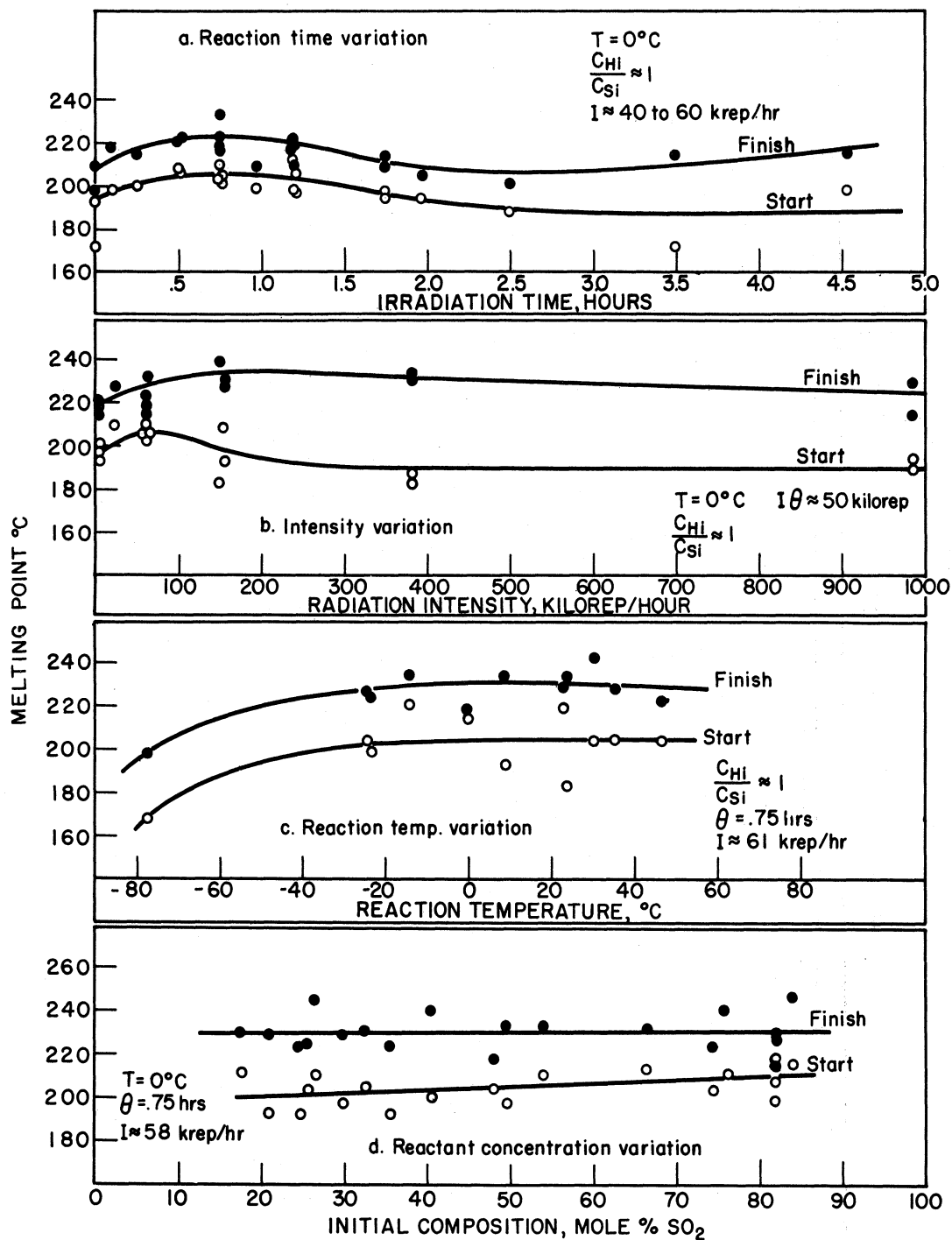


Figure 4. Melting Points of the n-Hexene-1, Sulfur Dioxide Copolymers as a Function of: (a) Reaction Time, (b) Radiation Intensity, (c) Reaction Temperature, and (d) Initial Reactant Composition.

in the reacting system had little or no effect on the melting temperature of the hexene-1 copolymers. As shown in Figure 4d, the softening temperature increased very slightly with increasing sulfur dioxide concentration in the reaction mixture.

Density of the copolymers was not affected by reaction time or radiation dose. There was very little effect of radiation intensity, reactant concentration, or reaction temperature on the densities of the hexene-1 sulfur dioxide copolymers.

Tensile strengths and elongations were measured on three molded copolymers produced at three different radiation doses from each of the butene-1, hexene-1, decene-1, and dodecene-1 sulfur dioxide systems. Tensile strengths increased slightly with increasing time of reaction for the hexene, decene, and dodecene copolymers. The tensile strengths of the molded butene-1 copolymers decreased with increasing reaction times. The elongations for the butene-1, hexene-1, and dodecene-1 copolymers go through maximum values in the range of reaction time studied. The elongations of the decene-1 copolymers decreases with increasing reaction time.

The softening points, densities, and tensile strengths of the copolymers decreased with increasing molecular weight of the olefin reactant. Snow and Frey⁽¹⁴⁾ found that the physical properties of the polysulfones produced by peroxide initiation were inverse functions of the reactant hydrocarbon molecular weight. Crouch and Wicklatz⁽²⁾ confirmed this fact in emulsion polymerization conditions. The behavior was the same using gamma radiation initiation conditions.

In order to make intrinsic viscosity measurements on the copolymers, it was necessary to find solvents for the copolymers produced by gamma radiation reaction initiation. After reviewing the literature for solvents used by others in making similar measurements and after conducting a series of solubility tests on various radiation produced polysulfone products, it was found that no single

ordinary solvent was satisfactory for the polysulfones investigated here. In general, it was found that the polysulfones from low molecular weight hydrocarbons were soluble in highly polar solvents, whereas high molecular weight hydrocarbon polysulfones were soluble in non-polar solvents. No solvent was found to dissolve the ethylene, propylene, or isobutylene polysulfones produced under gamma radiation. Table IV is the qualitative results of these solubility tests. No quantitative tests were made and only observations were recorded. The majority of the observations were merely "soluble" or "insoluble".

Solution viscosities of the decene-1, dodecene-1, and some of the hexene-1 polysulfones were made in tetralin while those for the butene-1, butene-2, and remaining hexene-1 polysulfones were made in pyridine. Specific viscosities were made at two or more solute concentrations, and the straight line thus obtained was extrapolated to zero concentration of solute to give the intrinsic viscosity characteristic of the polymer. This intrinsic viscosity is recorded in Table III. Several significant observations were made from the specific viscosity measurements. In all cases except in the dodecene-1-sulfur dioxide system, the copolymers which were produced at long reaction times and consequently high doses had lower intrinsic viscosities than the copolymers produced at the short times. It was found in the course of the solubility investigations that the dodecene-1 polysulfone produced at high radiation doses was not wholly soluble (Run 76, Table III). Long, fibrous-like material remained undissolved after standing several days in the tetralin solvent. No viscosity measurements were made on this partially soluble copolymer.

Table V is a summary of the ranges of physical properties determined in this study compared with the properties of the polysulfones produced by other means of reaction initiation. The values listed for this work are the highest and lowest values of Tables II and III for a particular compound. It may be seen that, in general, the values for the physical properties of the copolymers pro-

TABLE IV. SOLUBILITIES OF SOME POLYSULFONES PRODUCED BY GAMMA RADIATION INITIATION

Resin Solvent	Reaction Conditions:					Equimolar React. Comp.		
	T = 0°C	I = 40-65	kilorep hour	ss = slightly soluble				
	i = insoluble	s = soluble						
	Ethy- lene SO ₂	Propy- lene SO ₂	Butene-1 SO ₂	Butene-2 SO ₂	Isobuty- lene SO ₂	Hex- ene SO ₂	Decene-1 SO ₂	Dode- cene-1 SO ₂
Cyclohexane	i	i			i			
Oleic Acid	i	i						
Ethyl Alcohol	i	i	i	i	i	s	s	s
Tetralin	i	i			i			
Benzene	i	i			i	i	s	s
Decalin	i	i			i	s	s	ss
Anisole	i							
Propylene Glycol (1,2)		i			i	i	i	i
Amyl Alcohol		i			i	i	i	i
Cyclohexanone		i			i	s	s	s
2-Butanone	ss	i	s		i			
Acetone	ss	i	s		i	s		
Water	i	i	i		i	s		
Nitro Benzene								
Carbon Tetrachloride	i	i						
Chloroform	i	i			i			
Mixed Xylenes	i	i			i			
Diethyl Ether	i	i			i			
Toluene	i	i			i			
Petroleum Ether (55-65°)	i	i			i			
Sulfur Dioxide		s			i		i	i
Cyclopentanone		i			i			
50:50 H ₂ SO ₄ -HNO ₃	i	i			i			
Conc H ₂ SO ₄	i	s	s		i			
Pyridine	i	i	s	s	i	s		

TABLE V. COMPARISON OF POLYSULFONE PROPERTIES BETWEEN THIS WORK AND THE LITERATURE

Resin	Property	Softening Range °C		Intrinsic Viscosity -1 (grams/deciliter)		Density, gm/cm ³		Tensile Strength psi	
		Here	Literature	Here	Literature	Here	Literature	Here	Literature
1. Ethylene-SO ₂		312-341d	300-310d (17)*		1.67-1.74				
2. Propylene-SO ₂		258-283d	250d (12)	112.4 = $\frac{\eta_{sp}}{C}$ (17) .025 gm. moles in conc. H ₂ SO ₄ @ 20°C	1.44-1.58	1.49-1.51 (14)		1800-4000 (14)	
3. Butene-1-SO ₂		208-246		.123-.146 in acetone	1.30-1.60	1.35-1.40 (14) 1.376 (2)	5,210-7,700 6010 (2)		
4. Butene-2-SO ₂		223-258		.140-.150	1.40-1.60	1.30-1.36 (14)		2300-4500 (14)	
5. Isobutylene-SO ₂		233-262d	340d (12)		1.33-1.62				
6. Hexene-1-SO ₂		172-221	soft 100 (14)	1.30-2.00	1.11-1.20			2950-3130	
7. Decene-1-SO ₂		160-210	soft at (14) room temp.	3.00-3.40	1.05-1.06			1600-1680	
8. Dodecene-1-SO ₂		143-209		4.10	1.01-1.06			1120-1490	
9. 1-3 Butadiene-SO ₂		292-305d	200-220d (17)		71.2 = $\frac{\eta_{sp}}{C}$ (17) .025 gm. mole in conc. H ₂ SO ₄ @ 20°C				
10. Cyclopropane-SO ₂		140-148d							
11. Pentene-1-SO ₂			340 (14)			1.282 (13) 1.31 (14)		5340 (2) 2100-3190 (14)	
12. Octene-1-SO ₂			175-200 (14)					1490 (2)	

d denotes partial decomposition

* Numbers in parentheses refer to the bibliography

duced from gamma radiation were slightly higher than those reported in the literature for the same copolymeric material produced by other means. For example, Snow and Frey⁽¹⁴⁾ reported that the hexene-1-sulfur dioxide copolymer softened at 100°C whereas the radiation initiated copolymer had a softening, melting range of 172-221°C. The tensile strengths for the gamma radiation initiated copolymers were found to be higher than those reported in the literature. The butene-1-sulfur dioxide copolymer produced here had tensile strengths in the range of 5,210-7,700 psi, whereas a comparable copolymer was reported to have tensile strengths of 3,200-4,100 psi⁽¹⁴⁾ or 6,010 psi.⁽²⁾

THE EFFECTS OF GAMMA RADIATION ON SEVERAL
POLYSULFONE REACTIONS — PART II. KINETICS OF
THE REACTIONS

Introduction

The first paper in this two-part series described the various reactions of sulfur dioxide and olefins in the presence of gamma radiation. The physical properties of the products were presented as functions of the reaction conditions, i.e., radiation intensity and dose, temperature, and concentration of reactants.

This paper discusses the rates at which sulfur dioxide reacts with various olefins in a gamma radiation field. The kinetic data taken on several reactions have been correlated by an expression derived from the postulation of a free radical-type mechanism. A complete description of the interaction of radiation and the chemical reactants and the subsequent scheme of reactions is given in the following discussion.

A. MECHANISM OF THE POLYSULFONE REACTION

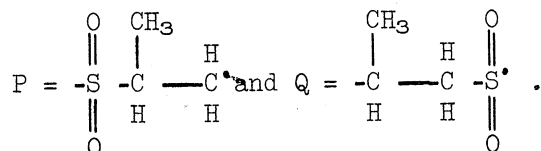
The treatment of the kinetics of the polysulfone reactions starts with the assumption that gamma radiation photons produce free radicals which initiate chain reactions. There are several ways in which free radicals may be produced by gamma photons. Those which are believed to be most important in the sulfur dioxide-hydrocarbon system are tabulated as follows:

- (1) The interaction of the gamma photons from Co-60 with the molecules of the system producing Compton electrons.
- (2) The ionization and excitation of molecules in the system by the Compton electrons in a thermalizing process.
- (3) The neutralization of the ionized molecules by thermalized electrons producing excited molecules.
- (4) The decomposition of the excited molecules producing free radicals.

H,S denote hydrocarbon or sulfur dioxide reactants.

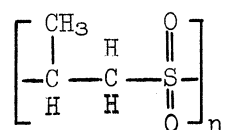
P,Q denote active hydrocarbon and sulfur dioxide radical reacting ends respectively of the polymerizing molecules.

For example, in the case of propylene sulfur dioxide reaction,



R is an initiation rate function.

X represents dead polymer, i.e.,



p,d,t subscripts represent propagation, depropagation, and termination processes.

m,n subscripts signify molecular order corresponding to arbitrary molecular weights of the reacting molecule.

It should be pointed out that an individual molecule may be reacting at each end by the proposed reaction scheme.

Applying the usual mathematical treatment to the above reaction scheme, equations were derived which represented the time behavior of both the reactant and radical concentrations in the reaction mixture in the radiation field. In this treatment the following assumptions were made:

(1) Reactions 3 through 9 had first order dependence on each of the reactant concentrations.

(2) Net production of P-type radicals equalled the net production of Q-type radicals, since the product had an alternating -H-S-H-S structure.

(3) The reaction rate constants were independent of molecular order (size).

The two simultaneous differential equations which kinetically describe the hydrocarbon-sulfur dioxide polysulfone reactions are,

$$\frac{dC_R}{d\theta} = R_H + R_S - C_R^2 \frac{k_{t,HH}k_{p,SH}^2(C_H^{\alpha})}{2k_{t,HS}k_{p,HS}k_{p,SH}(C_H^{\alpha})(C_S^{\beta}) + k_{t,SS}k_{p,HS}^2(C_S^{\beta})^2} + \frac{2k_{t,HS}k_{p,HS}k_{p,SH}(C_H^{\alpha})(C_S^{\beta}) + k_{t,SS}k_{p,HS}^2(C_S^{\beta})^2}{[k_{p,SH}(C_H^{\alpha}) + k_{p,HS}(C_S^{\beta})]^2} \quad (10)$$

and

$$\frac{dC_H}{d\theta} + \frac{dC_S}{d\theta} = - (R_H + R_S) - 2k_{p,HS}k_{p,SH}C_R \left[\frac{C_S C_H - \alpha\beta}{k_{p,SH}(C_H^{\alpha}) + k_{p,HS}(C_S^{\beta})} \right] \quad (11)$$

where,

C_H, C_S are the hydrocarbon and sulfur dioxide concentrations, respectively,

C_R is the total radical concentration,

d is the differential operator,

θ represents time,

α, β are defined to be $\alpha = \frac{k_{d,HS}}{k_{p,SH}}$ and $\beta = \frac{k_{d,SH}}{k_{p,HS}}$.

As they now appear, the equations cannot be solved rigorously by ordinary analytical methods for the reactant and the radical concentrations as functions of time. With certain simplifying assumptions, approximate solutions may be obtained which represent the experimental data.

B. TOTAL DOSE CORRELATIONS

All of the experimental data involving the effects of gamma radiation on the polysulfone reactions were initially taken at approximately equimolar hydrocarbon to sulfur dioxide reactant concentrations (i.e., $C_{H1} = C_{S1}$), except

for the runs numbered 300 in the hexene-1-SO₂ reaction system. Since the product analysis showed an alternating equimolar structure of hydrocarbon to sulfur dioxide, at any time θ the instantaneous reactant concentrations were equal (i.e., $C_H = C_S$) and the rates of monomer removal from the reaction mixture were equal (i.e., $\frac{dC_H}{d\theta} = \frac{dC_S}{d\theta}$). Since high molecular weight products were formed in the course of the reactions, molecular orders m and n of equations (6) through (9) were apparently large numbers, at least of the order of 10². Thus, it may be assumed that the depropagation reactions played a relatively minor role in the reaction scheme. This means that α and β were either small enough to be neglected entirely or, that they were of the same order of magnitude so as to be considered equal. The assumption was also made that the initiation of radicals in reactions 1 and 2 was only a function of the radiation intensity I , i.e., $R_H + R_S = I(R_{IH} + R_{IS})$. Substituting these simplifications, the expressions (10) and (11) become

$$\frac{dC_R}{d\theta} = k_1 I - k_3 C^2 R, \quad (12)$$

$$\frac{dC_S}{d\theta} = \frac{k_1}{2} I - k_2 C R \left[\frac{C^2 S - \alpha \beta}{C_S + \beta} \right], \quad (13)$$

where

$$k_1 = k_{IH} + k_{IS}, \quad (14)$$

$$k_2 = \left[\frac{k_{pHS} k_{pSH}}{k_{pHS} + k_{pSH}} \right], \quad (15)$$

$$k_3 = \left[\frac{k_{tHH} k_{pSH}^2 + 2k_{tHS} k_{pHS} k_{pSH} + k_{tSS} k_{pHS}^2}{(k_{pHS} + k_{pSH})^2} \right]. \quad (16)$$

Equation (12) may be solved for C_R as a function of time by the usual methods, knowing the boundary condition that at time zero the radical concentration is also zero. The solution for equation (12) is:

$$C_R = \sqrt{\frac{k_1 I}{k_3}} \left(\tanh \sqrt{k_1 k_3 I} \theta \right) \quad (17)$$

The result states that the radical concentration builds from zero concentration to some finite constant value depending on the value of the constants and the square root of the radiation intensity. The rate of approach to this finite value is also dependent on the same constants and also to the square root of the intensity.

One further simplification may be made to equation (13) before solving it. Since the molecular weight of the experimental polymer was high, several hundred monomer units were removed in the propagation steps for each radical initially formed by radiation initiation. Thus, the initiation term may be neglected in solving equation (13) for reactant concentration as a function of the time.

Substituting equation (17) into equation (13), the solution for either reactant concentration as a function of time is:

$$C_S = \frac{C_{Si} - \beta}{[\cosh \sqrt{k_1 k_3 I} \theta] \frac{k_2 k_3}{k_2 k_3}} + \beta \quad (18)$$

where the assumptions and conditions that were made are:

- (1) $C_{Si} = C_{Hi}$,
- (2) Initiation term small in comparison with the monomer removal propagation term,
- (3) $\alpha = \beta$,
- (4) Initiation a function of radiation alone,
- (5) No wall or inhibitor termination,
- (6) Rate constants independent of molecular size.

In the experimental loading procedure it was impossible to load exactly an equimolar ratio of hydrocarbon to sulfur dioxide to the reactors. For this reason it was found convenient to handle equation (18) in a slightly different form for correlation of the experimental data. Dividing equation (18) by the original reactant concentration C_{Si} ,

$$\frac{C_S}{C_{Si}} = \frac{1 - \frac{\beta}{C_{Si}}}{[\cosh \sqrt{k_1 k_3 I} \theta] \frac{k_2/k_3}{k_2/k_3}} + \frac{\beta}{C_{Si}} \quad (19)$$

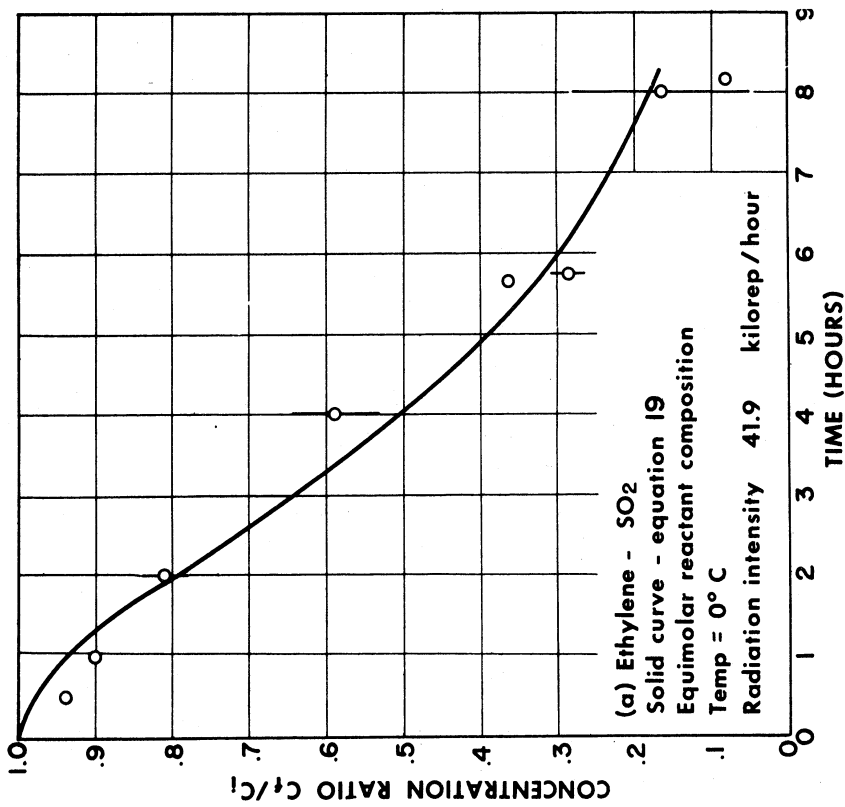
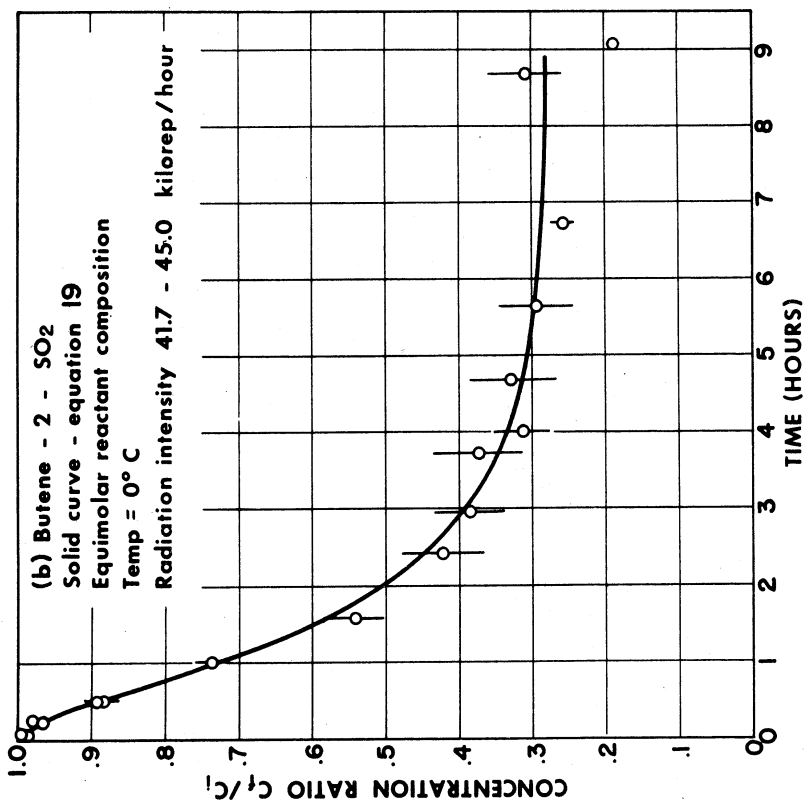


Figure 5. Concentration vs. Time for Some Polysulfone Reactions at 0° C, (a) Ethylene-SO₂, (b) Butene-2-SO₂.

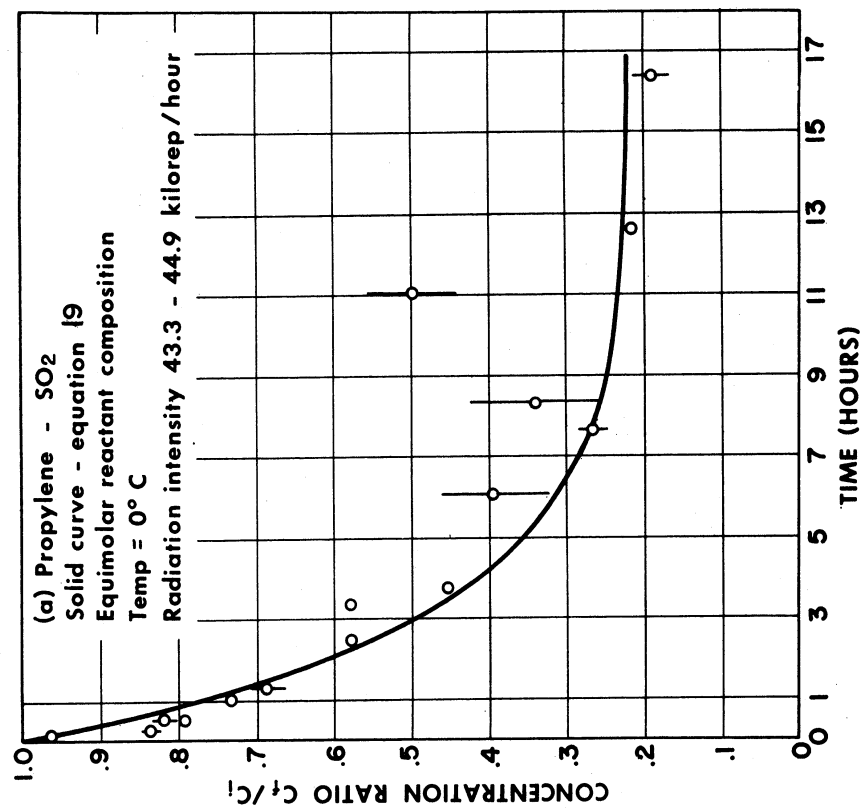
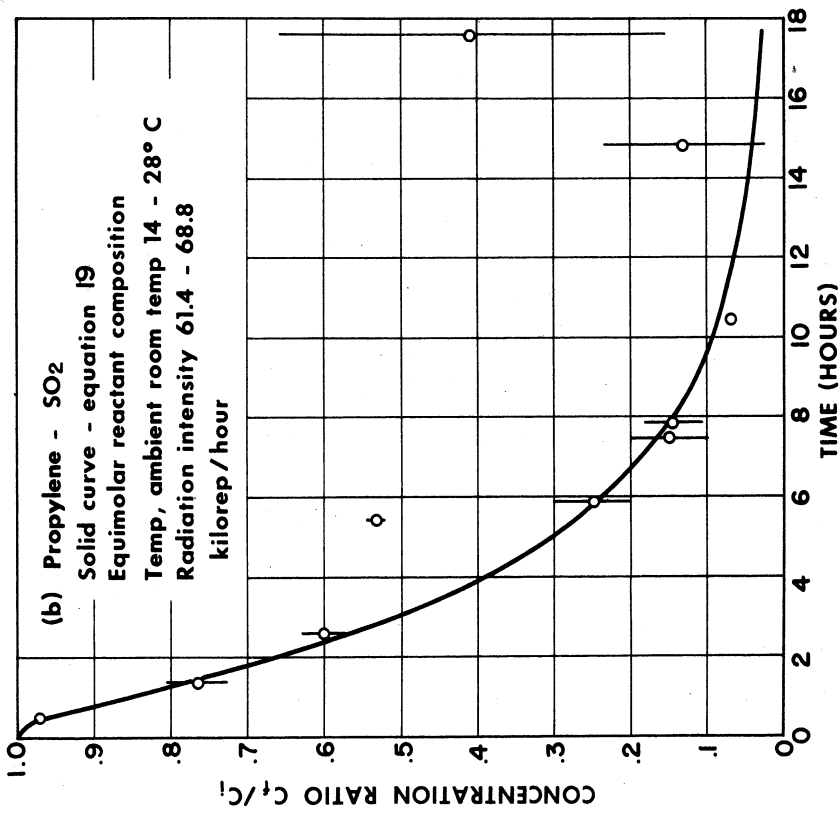


FIGURE 6 Concentration vs. Time for the Propylene-SO₂ Reaction at,
 (a) 0° Centigrade, (b) Ambient Room Temperature.

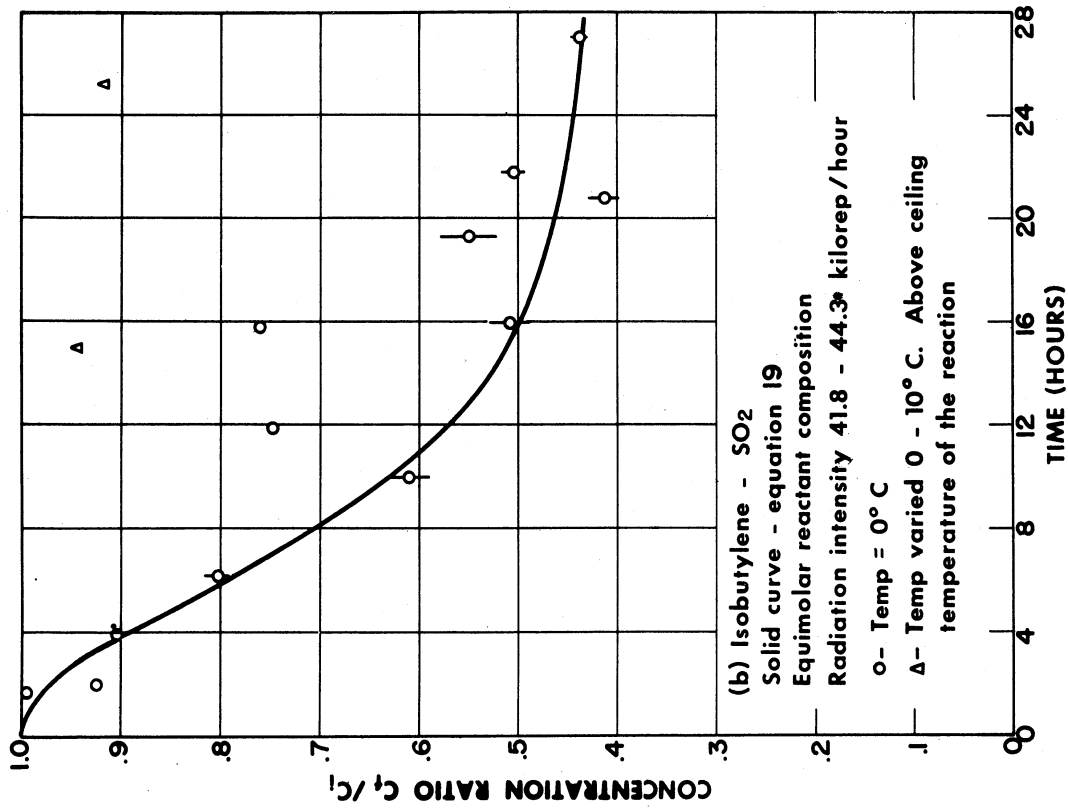
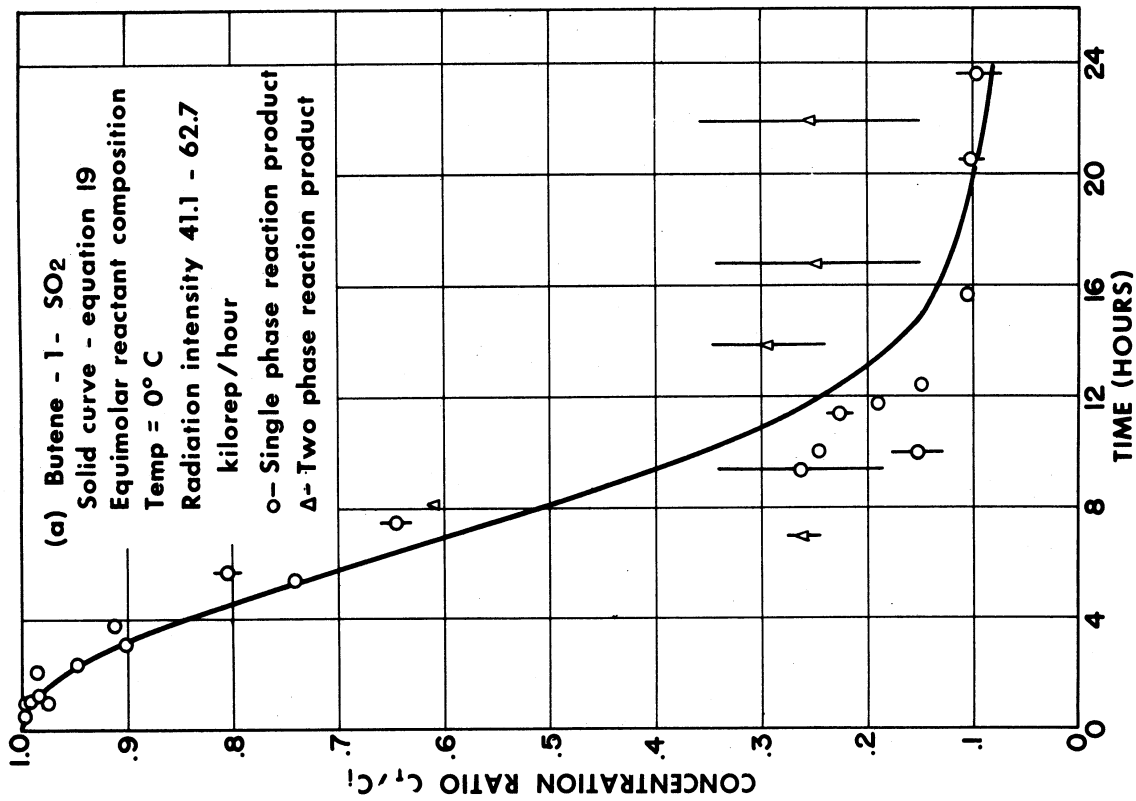


Figure 7. Concentration vs. Time for Some Polysulfone Reactions at 0° C. (a) Butene-1-SO₂, (b) Isobutylene-SO₂.

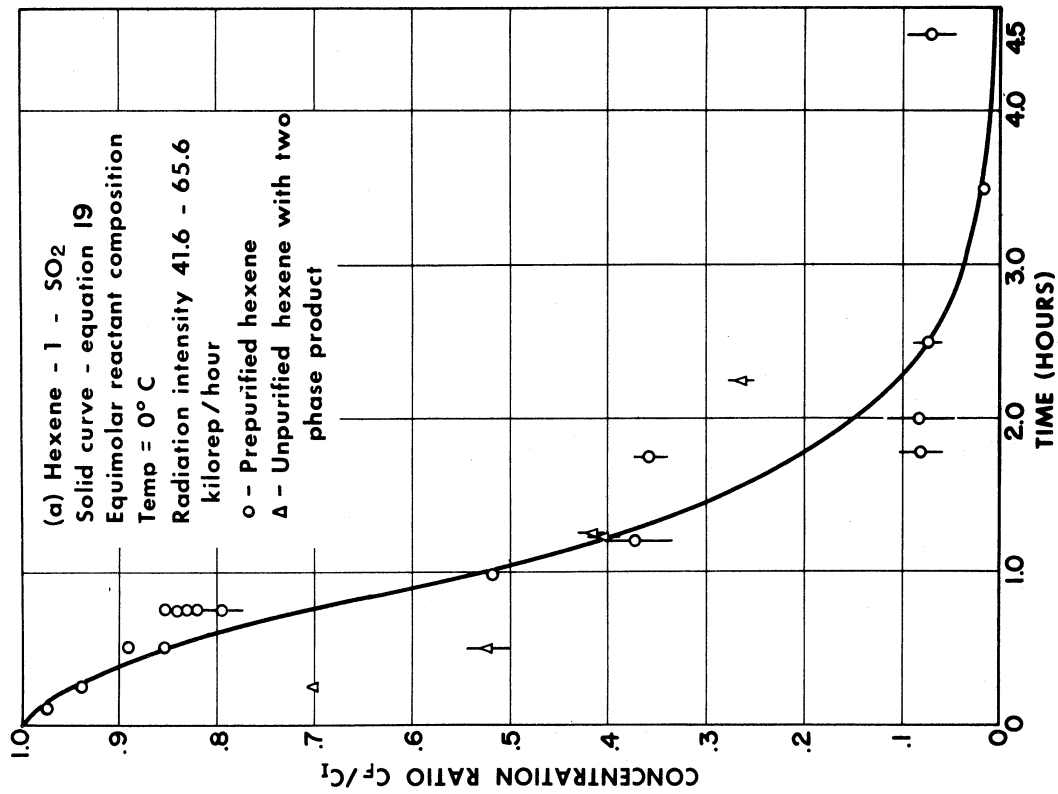
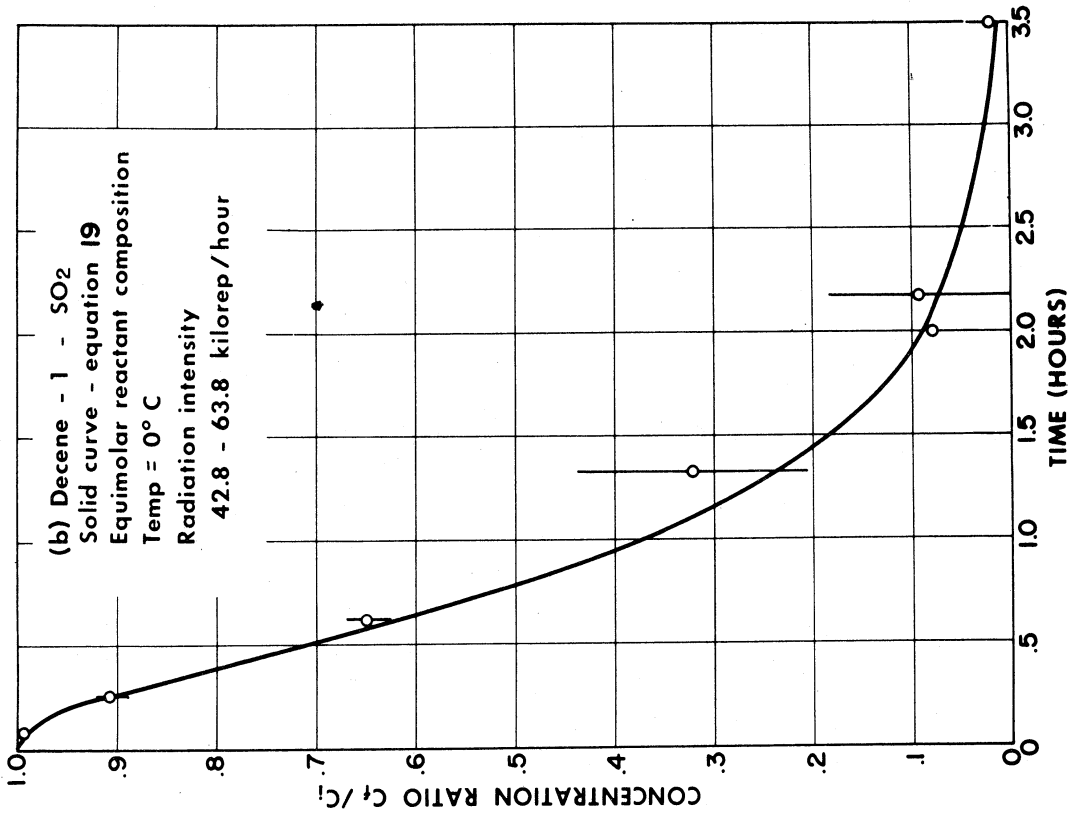


Figure 8. Concentration vs. Time for Some Polysulfone Reactions at 0° C. (a) Hexene-1-SO₂, (b) Decene-1-SO₂.

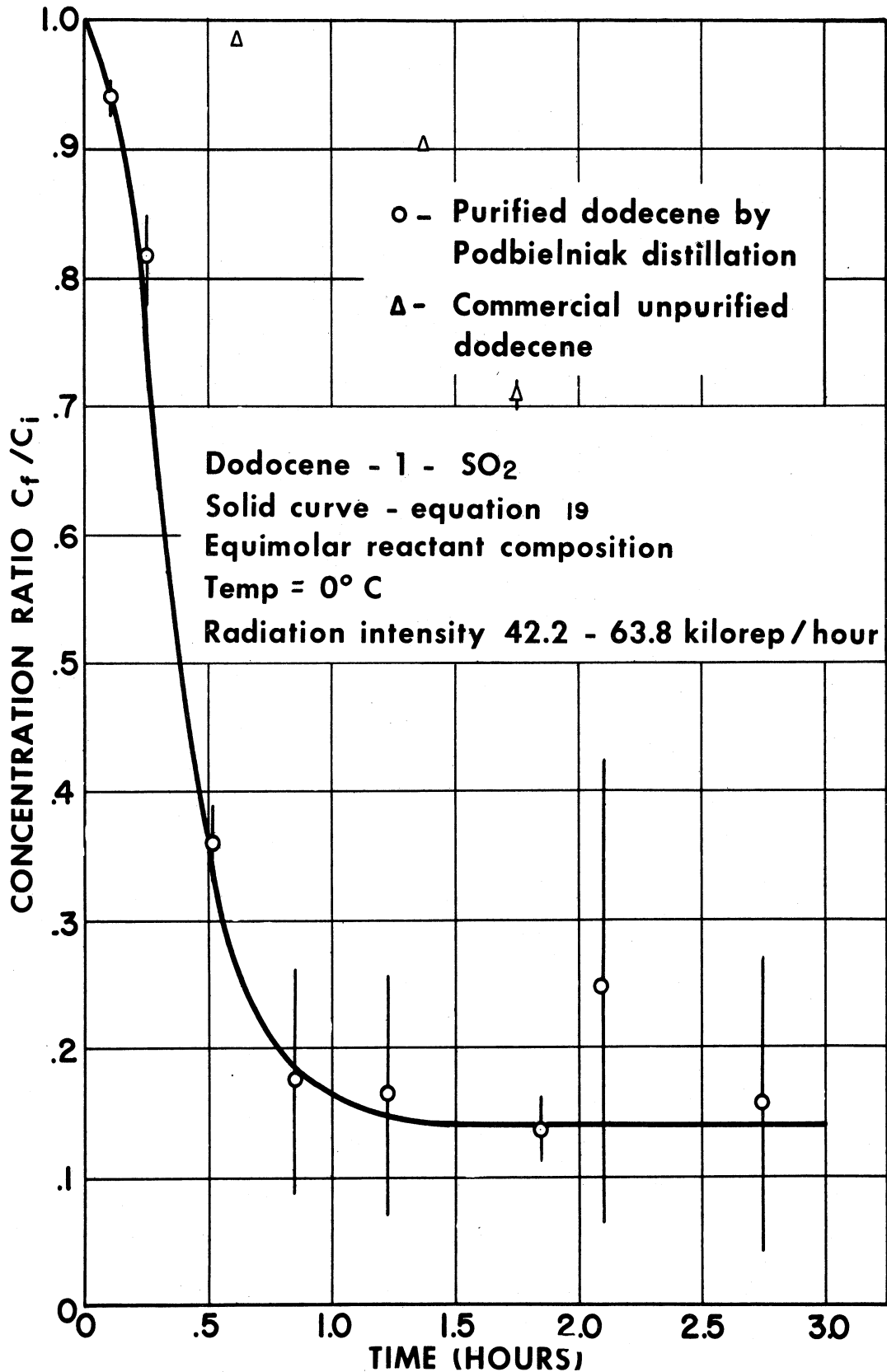


FIGURE 9 Concentration vs. Time for the Dodecene-1-SO₂ Reaction at 0°C.

In Figures 5 through 9, the average concentration ratio is plotted versus time θ for each of the olefin hydrocarbon-sulfur dioxide systems investigated. The vertical lines from these average data points represent the error in exactly loading an initial equimolar ratio of hydrocarbon to sulfur dioxide. The best fit as represented by equation (19) is plotted as the solid curve on the same figures. The values determined for the constants of equation (19) for these correlations are listed in Table VI. The constants were determined by trial and error application of equation (19) to the data. The values listed represent the best values obtained after a series of calculations. No correlation based on least squares or other correlation methods was possible because of the nature of the derived expression. The correlations are considered quite valid for most engineering applications of the data. They also constitute an indirect proof of the proposed mechanism of the reaction. Apparently all of the polysulfone reactions proceed by this mechanism with a variation in reaction-rate constants depending on the particular hydrocarbon employed in the reaction system.

The primary errors in the correlation of the data lie in the fact that there was some variation in experimental conditions. The radiation intensity received by an experimental run of a single hydrocarbon series was, in general, a function of time. The constants presented in Table VI were calculated for the average radiation intensity for a single hydrocarbon system even though the intensity varied by sometimes as much as 1.5 in the individual runs of the system. This intensity was critically dependent on distance from the source. Although the positions of the reactors with relation to the source were determined for each run, an exact duplication between runs was difficult. In the runs of longer duration, the source was raised and lowered several times during the course of a run by persons investigating other problems in a radiation field. The effects of this intermittent raising and lowering of the source on the reaction are unknown.

TABLE VI. CORRELATION CONSTANTS FOR THE POLYSULFONE REACTION SYSTEMS

Hydrocarbon Investigated	Reaction Temp. °C	Maximum Variation of Initial Reactant Conc'n. moles H / mole S	Calc. 1:1 Initial Reactant Conc'n. moles / liter	Radiation Intensity Range kilorep/hr.	$\sqrt{k_1 k_3 I}$ / hr.	Correlation Constants of Equation 19.			Figure No.	
						$\frac{\beta}{CS_1} = \frac{\alpha}{CH_1}$	$\frac{k_2}{k_3}$	$\frac{\beta}{\sqrt{k_1 k_3}} = \frac{\alpha}{(k_{rep} \cdot hr)^{.5}}$		
Ethylene	0	.895-1.37	7.88	41.9	.50	.52	0	.077	0	5a
Propylene	0	.840-1.28	8.20	43.3-44.9	35.	.01	.22	5.3	1.80	6a
Propylene	Ambient Room 14-28	.876-1.40	7.80	61.4-68.8	1.4	.194	.02	.17	.16	6b
Butene-1	0	.905-1.32	7.38	41.1-62.7	.031	25.	.08	.0043	.59	7a
Butene-2	0	.974-1.38	7.50	41.7-45.0	2.0	.35	.28	.30	2.10	5b
Isobutylene	0	.885-1.12	7.38	41.8-44.3	.16	1.1	.43	.024	3.18	7b
Hexene-1	0	.855-1.14	6.01	41.6-65.6	1.13	.5	0	.155	0	8a
Decene-1	0	.720-1.42	4.34	42.8-63.8	2.25	.63	0	.31	0	8b
Dodecene-1	0	.648-1.095	3.81	42.2-63.8	2.77	1.76	.14	.38	.53	9
Cyclopropane	0	1.19 -1.57	8.92	42.8-44.1	Not correlated					10

Other, more obvious, inconsistencies in the investigations were apparent from observations of the reaction product, reactant purity, etc. These observations are recorded in the column headed "Remarks" in Table II. These inconsistent data points are shown in the Figures with different symbolic notation and were not taken into consideration in the correlation procedure.

The reaction systems for all dodecene-1, sulfur dioxide runs were two phase liquids. The effect of two liquid phases on the reaction is not known. Probably true reaction rates were not measured over portions of the concentration range because, presumably, diffusion of the reactants from one phase to the other would control the reaction after some finite reaction time. Since the product in all cases was an equimolar proportion of the two reactants, and since high yields were obtained in fairly short times, this effect may not have been extremely important.

In the case of the copolymerization of cyclopropane with sulfur dioxide, no attempt was made to handle the experimental data by means of equation (19) because the data indicated somewhat of a variation from the assumptions and the mechanism of reaction leading to the correlation. Single sulfur analysis on each of two samples where there was enough product for testing indicated a deviation from a one-to-one cyclopropane to sulfur dioxide ratio in the product, as indicated in Table II. The decomposition point of the product was considerably lower than those of the polymers which contained comparable molecular weight hydrocarbon reactants. The product yield was extremely small. From these considerations it was concluded that a polymer of high molecular weight was not produced in the cyclopropane sulfur dioxide reaction as was the case in the other polysulfone reactions. Although no direct measurements were made, it was considered possible that the propagation reaction was terminated before large molecular weights were obtained. Another possibility is that, since cyclopropane is a different class than the rest of the hydrocarbons investigated here, it

may not react with sulfur dioxide by the proposed reaction scheme at all. The data obtained for the reaction are shown in Figure 10 as the grams of product formed per liter of reacting mixture as a function of time. The curve shown is not a mechanistic correlation but only a curve through the data points.

C. HEXENE-1-SULFUR DIOXIDE REACTION

To investigate the effects of reaction temperature, radiation intensity, and reactant concentration on the rate of the hexene-1-sulfur dioxide reaction, runs were made in which each of these quantities was varied separately while the others were held constant. Table VII gives the range of each variable investigated for the reaction.

1. The Effect of Reaction Temperature

For any mechanistic scheme such as that represented by reactions (1) through (9), the reaction rate constants must be assumed to vary independently with temperature. Thus, the defined quantities α and β must be assumed to be functions of temperature. Although they were found to be approximately equal to 0 at 0° Centigrade, there may be a temperature at which they become quite appreciable in relation to the other terms. If the temperature dependence of α and β are the same, i.e. $\alpha = \beta$ for any temperature, then the development of equations (12) and (13) are the same. Substituting equation (17) for the radical concentration as a function of time, equation (13) becomes

$$\text{Rate} = \frac{dC_S}{d\theta} = - k_2 \sqrt{\frac{k_1 I}{k_3}} \left[\tanh \sqrt{k_1 k_3 I} \theta \right] [C_S - \alpha]. \quad (20)$$

At 60.5 kilorep per hour for .75 hours and at average concentration conditions equation (20) becomes,

$$\frac{\text{Rate avg}}{C_S \text{ avg.}} = 7.78 k_2 \sqrt{\frac{k_1}{k_3}} \left[\tanh 5.84 \sqrt{k_1 k_3} \right] \left[1 - \frac{\alpha}{C_S \text{ avg.}} \right] = f\left(\frac{1}{I}\right) \quad (21)$$

Some general conclusions on the temperature dependence of the reaction may be drawn by looking at Figure 11, where the logarithm of the average rate of disappearance of either reactant monomer divided by the mean average re-

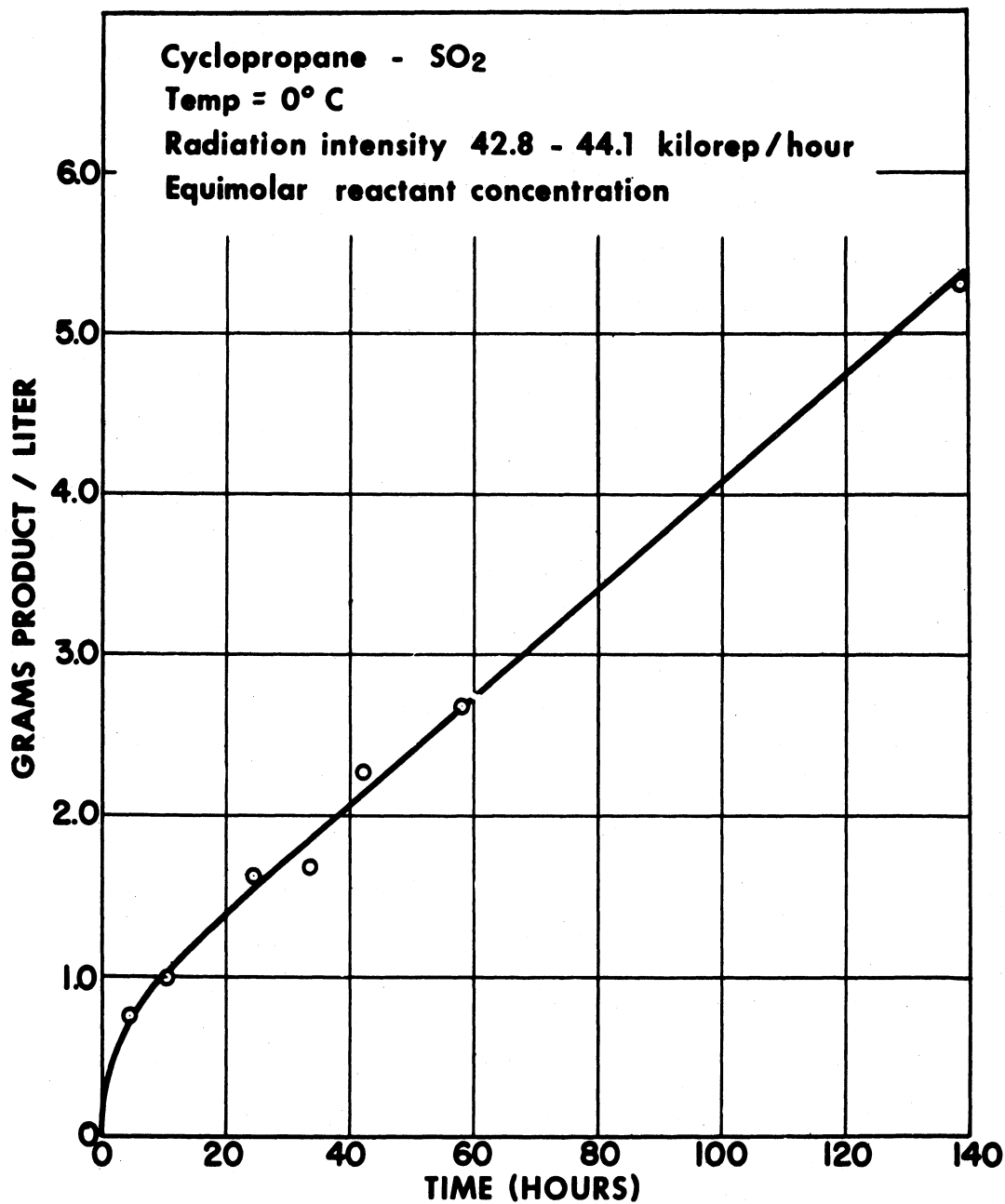


FIGURE 10 Rate of Appearance of the Cyclopropane-SO₂ Reaction Product.

TABLE VII. Range of Experimental Conditions for the Hexene-1 Sulfur Dioxide Reaction

Run Numbers	Temperature Range °C	Initial Conc. Range Moles H/mole S	Time of Reaction hours	Radiation Intensity Krep/hr.	Radiation Dose Kilorep	Figure Numbers
54-122	0	Approx. 1.	0-4.53	41.6-65.6	0-188.	8a
200-210	-77.3 to 46.3	Approx. 1.	.750	58.8-62.2	44.1-46.7	11, 12
300-327	0	.187-5.69	.200-.750	57.0-62.2	11.4-46.7	14, 15
400-412	0	Approx. 1.	.0583-17.72	3.58-987	42.7-69.9	13

actant concentration is plotted as an inverse function of the absolute reaction temperature. The numerical value of equation (21) for the hexene-1-sulfur dioxide reaction plotted in this manner, goes through a maximum value at about 19.5°C. From about -24 to +9.5°C $\left[\frac{1}{T} \text{ varying from } 3.54 \text{ to } 4.1 \text{ (x}10^{-3}\text{)} \right]$, the curve is nearly a straight line indicating that the combination of reaction rate constants obeys the Arrhenius temperature relationship in this range. It may be pointed out that in this region the depropagation reactions (5) and (6) are probably negligible and $\alpha = \beta$ as previously discovered for the runs made at 0°C.

The upward curvature in the low temperature range is to be expected in chemical reactions activated by gamma radiation (see, for example, reference (11), Progress Report 5, pages 36-40). Although k_2 and k_3 were assumed independent of radiation in the development of the correlation mechanism, k_1 was considered to be dependent on the radiation. As the values of k_2 and k_3 decrease with decreasing temperature, the overall rate of the reaction becomes more dependent upon the initiation steps. This will also explain the observed lower-melting points and lower-molecular weight of the copolymers produced at the lowest reaction temperature. Apparently the rate of the propagation (and possibly termination) were reduced to such a point that only a relatively few reactant molecules were able to combine with each initiated reaction center produced by the radiation.

One other conjecture may be made about the temperature behavior of the reaction from the Figure. Above 9.5°C ($\frac{1}{T} = 3.5 \times 10^{-3}$), the depropagation reaction apparently become significant in the reaction scheme. At this temperature, although α was assumed to be equal to β , they were probably no longer negligible in the correlation and the curvature is presumably indicative of α and β increasing with temperature in some manner.

From the arithmetic plot of average rate of monomer disappearance vs. temperature shown in Figure 12, extrapolation of the curve to zero rate gave the ceiling temperature for the hexene-1-sulfur dioxide reaction. This

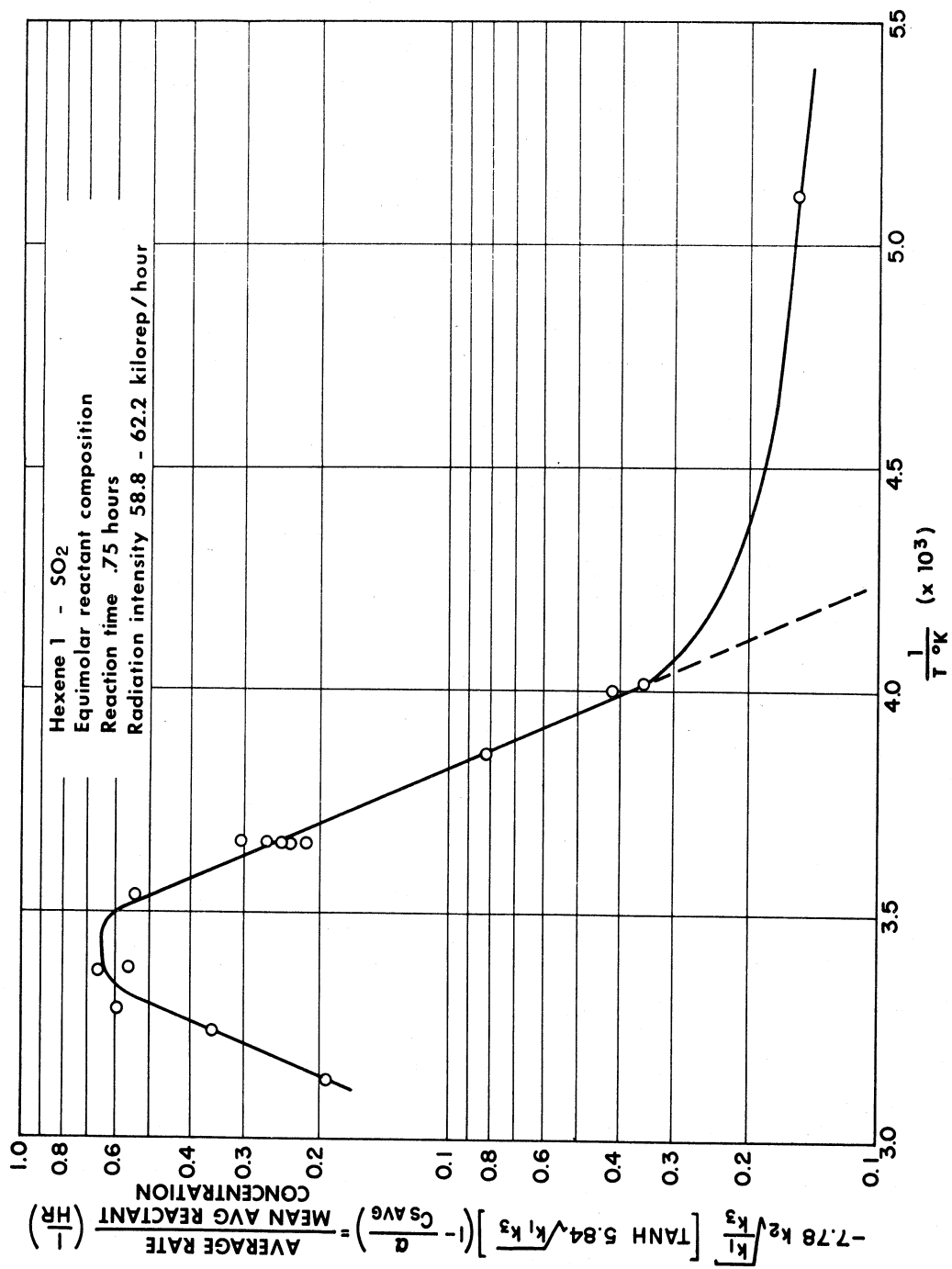


FIGURE 11 Effect of Temperature on the Hexene-1 Sulfur Dioxide Reaction.

ceiling temperature (the temperature above which the reaction does not occur), was found to be 57°C. Grassie⁽⁸⁾ reported the value of the ceiling temperature for the hexene-1-sulfur dioxide reaction as 59.0°C.

2. The Effect of Radiation Intensity.—The experimental conditions for all runs where radiation intensity was varied were 0°C. and equimolar reactant concentration.

Since α and β were assumed independent of intensity and were found to be negligible at a reaction temperature of 0°, they were presumably negligible for all runs where radiation intensity was varied. The value of $\sqrt{k_1 k_3}$ determined from previous treatment of the integrated rate expression was found to be $.155 \frac{1}{\text{kilorep}^{.5} \text{ hr}^{.5}}$ at 0°C. Substituting these values into equation (20) at the average conditions gives:

$$\frac{\text{Rate avg.}}{(C_{\text{avg.}})^{(\tanh .155 I^M \theta)}} = -k_2 \sqrt{\frac{k_1}{k_3}} I^M \quad (22)$$

Because the radiation intensity appears in both the multiplier and the argument of the hyperbolic tangent, the method of successive approximations was applied to equation (22) to calculate the exponent of the intensity. The intensity exponent M was assumed in the argument of the hyperbolic tangent and the value for the left side of the equation was calculated for each data point. The slope of the line determined by the logarithms of these calculated values plotted, versus the logarithms of the respective intensities, was taken for the second approximation. This procedure was repeated until the slope of the line was the same as the assumed value in the tanh term. The calculations converged rapidly to an exponent of .75 on the radiation intensities. A graph of equation (22) with M = .75 is shown in Figure 13.

This exponent of .75 for the initiation factor is somewhat greater than the .5 value predicted by equation (20); however, it agrees with the experimental values found by other experimenters working on similar polysulfone

reactions. Dainton and Coworkers (1,3,4,5) observed that the initiation exponents for the copolymerization of sulfur dioxide with various olefinic materials varied from .51 to .80 with ultra violet light and beta particle initiation.

3. The Effect of Reactant Concentration.--A re-examination of the equations and assumptions leading to the correlation of the data is necessary when the initial reactant composition is varied appreciably from the equimolar hydrocarbon to sulfur dioxide proportions that were used during the bulk of this work.

Since C_{Hi} no longer may be assumed to equal C_{Si} , equations (10) and (11) no longer simplify to equations (12) and (13) but rather to:

$$\frac{dC_R}{d\theta} = k_1 I - C_R^2 \left[\frac{k_{t,HH} k_{p,SH}^2 C_H^2 + 2k_{t,HS} k_{p,HS} k_{p,SH} C_H C_S + k_{t,SS} k_{p,HS}^2 C_S^2}{[k_{p,SH} C_H + k_{p,HS} C_S]^2} \right] \quad (23)$$

and

$$\frac{dC_H}{d\theta} = \frac{dC_S}{d\theta} = -k_{p,HS} k_{p,SH} C_R \left[\frac{C_S C_H}{k_{p,SH} C_H + k_{p,HS} C_S} \right]. \quad (24)$$

It is seen from equation (24) that if

$$\frac{C_R}{k_{p,SH} C_H + k_{p,HS} C_S}$$

was a constant over the range of reactant concentrations investigated, the rate of disappearance of either reactant was proportional to the concentration of each reactant to the first power. The curve described by the logarithm of average rate divided by the average concentration of one reactant as a function of the logarithm of the average concentration of the other reactant should be a straight line with a slope of unity if this observation is correct. Figures 14 and 15 are graphs of the data which were plotted in this manner. Figure 14 is a graph of the $\log. \frac{\text{Rate}_{\text{avg.}}}{C_S \text{ avg.}}$ vs. $\log. C_H \text{ avg.}$ and Figure 15 is a graph of the $\log. \frac{\text{Rate}_{\text{avg.}}}{C_H \text{ avg.}}$ vs. $\log. C_S \text{ avg.}$

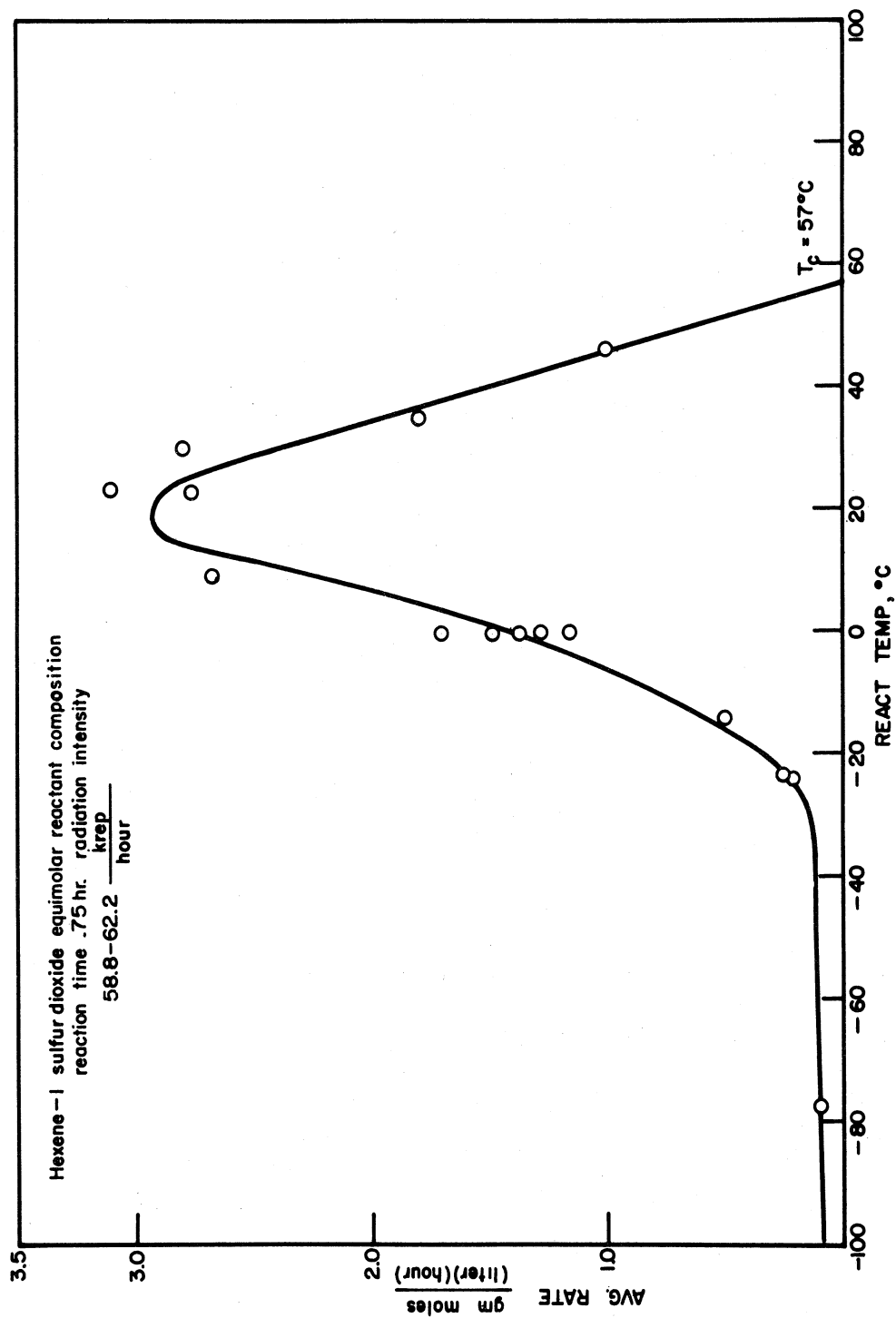


FIGURE 12 Rate of Monomer Disappearance as a Function of Reaction Temperature for the Hexene-1, Sulfur Dioxide Reaction.

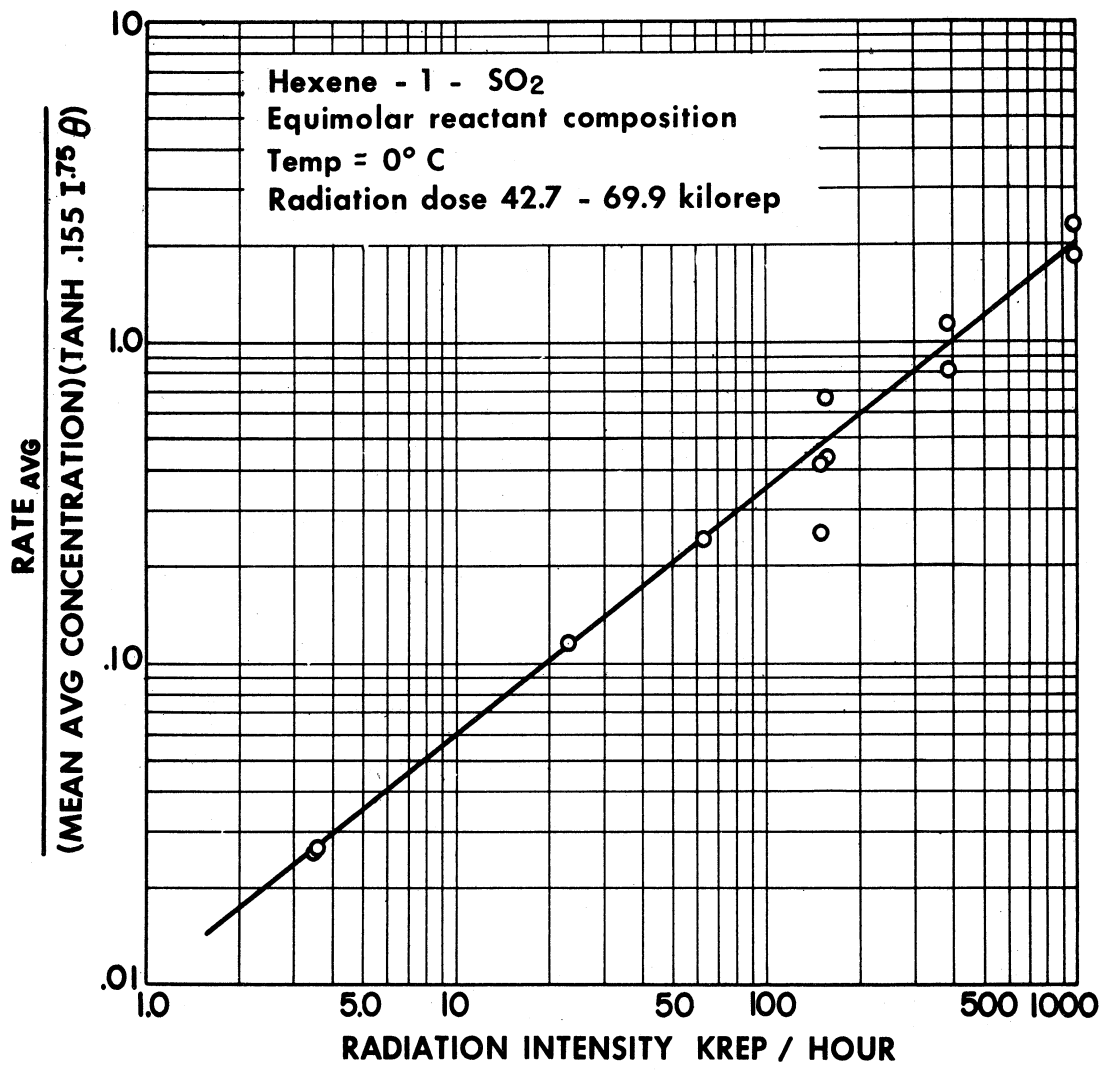


FIGURE 13 Effect of Radiation Intensity on the Hexene-1, Sulfur Dioxide Reaction.

The slopes of the lines determined by the data were nearly unity (in Fig. 14, slope = 1.1; in Fig. 15, slope = .96) in the high sulfur dioxide concentration regions, as shown in both figures. This indicated that the rate of the hexene-1-sulfur dioxide reaction was proportional to the product of the reactant concentrations, each raised to the power 1 in the region of high sulfur dioxide and low hexene concentration (i.e., $\frac{C_S}{C_H} > 1$). In the region of low sulfur dioxide and high hexene concentration no such correlation was apparent. Only general observations can be made from the data.

It was noticed in Figure 15 that in the low sulfur dioxide region (and high hexene-1 region), the parametric lines of constant $(\frac{C_F}{C_I})_S$ had slopes near 1.0 (See Table VII).

This fact and the observation of the sharp break in the curve of Figure 14 at a point just above an average hexene concentration of 6.0 moles/liter indicated that the reaction was less dependent upon the sulfur dioxide concentration at the high hexene concentrations.

Further attempts at correlation of the data were made with little results on which to base a sound conclusion. The most obvious discrepancy of the correlation procedure which could account for the observed irregular behavior of the reaction involves the examination of the assumption of constant $\frac{C_R}{k_{p,SH}C_H + k_{p,HS}C_S}$

The denominator will be examined first. It seems probable that the two propagation rate constants $k_{p,SH}$ and $k_{p,HS}$ are nearly equal. If these constants are equal, then this quantity may be factored from the denominator of equation (24) leaving the sum of the two reactant concentrations or the total concentration. From Table VIII it is seen that this total average concentration varied from 7.86 to 9.75 moles per liter for all runs conducted over the .75 hr. period. This variation does not explain the scatter of data in the low sulfur dioxide region of Figure 15. Acting on the basis that $k_{p,HS}$ was unequal

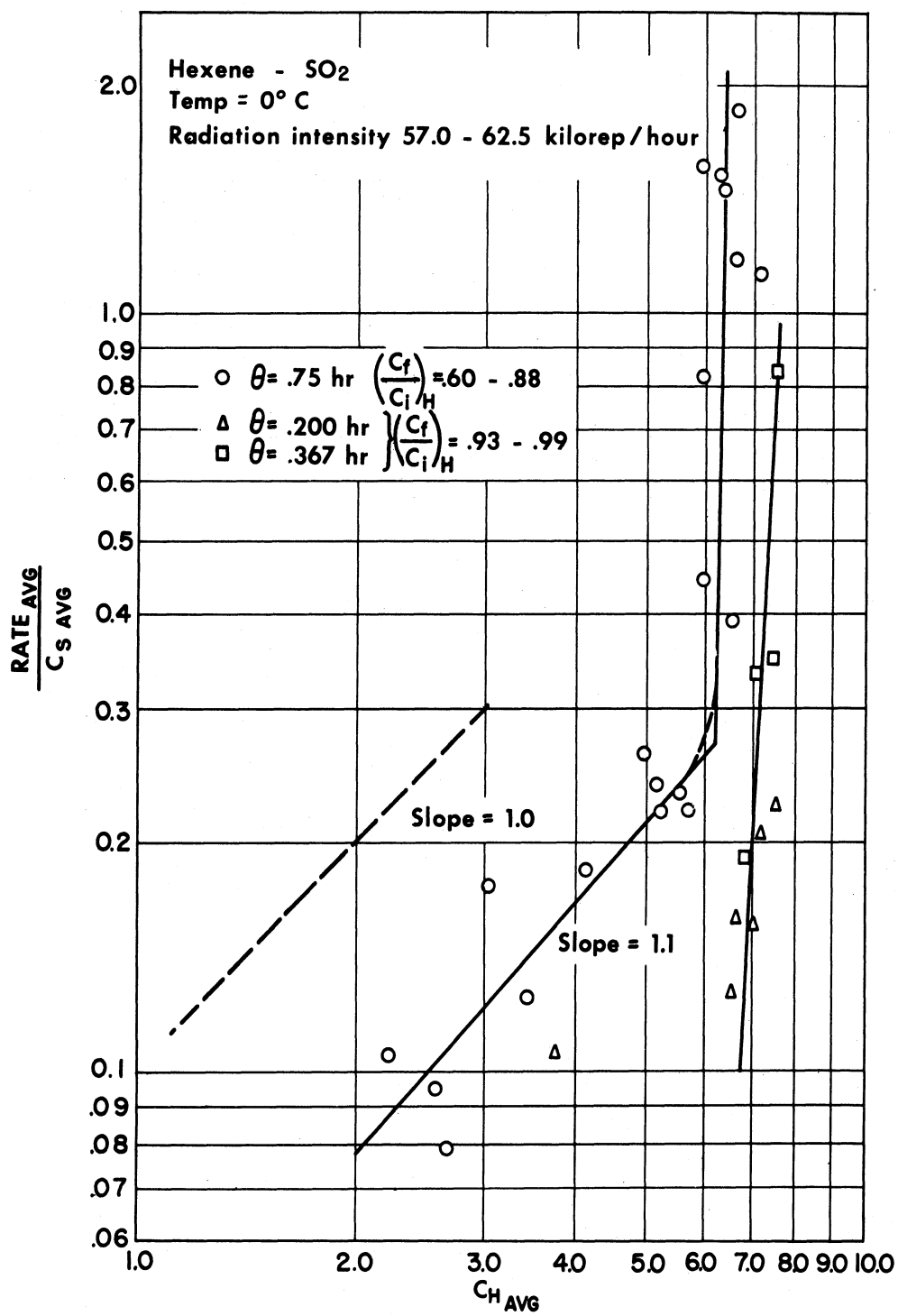


FIGURE 14 Effect of Hexene Concentration on the Rate of the Hexene-1, Sulfur Dioxide Copolymerization Reaction.

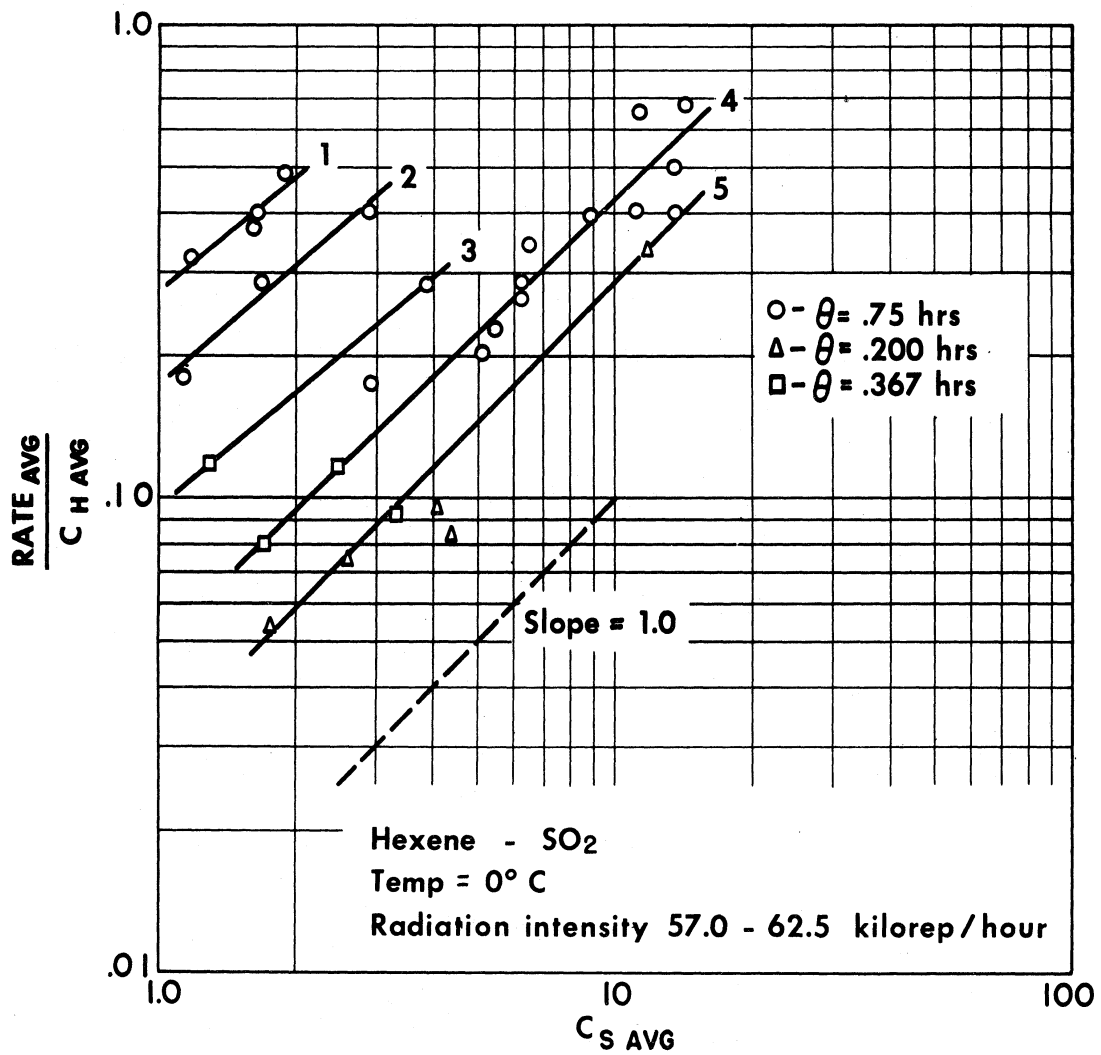


FIGURE 15 Effect of Sulfur Dioxide Concentration on the Rate of the Hexene-1, Sulfur Dioxide Copolymerization Reaction.

to $k_{p,SH}$, correlation of the data was attempted by assuming various ratios of $\frac{k_{p,HS}}{k_{p,SH}}$. This proved futile.

TABLE VIII
Parameters for the Curves of Figure 15

Curve No.	Slope	Variation of $\left(\frac{C_f}{C_i}\right)_S$	Variation of $(C_{S,avg.} + C_{H,avg.})$ $\frac{\text{gm.moles}}{\text{liter}}$	Reaction Time Intervals
1.	.80	.183-.292	7.86-8.03	.75 hr.
2.	.82	.407-.527	8.29-8.59	.75 hr.
3.	.79	.714-.736	8.72 9.75	.75 hr. .367 hr.
4.	.96	.821-.931	9.75-16.47 8.52- 9.57	.75 hr. .367 hr.
5.	.99	.932-.980	9.29-15.50	(.367 hr. (.200 hr.

Examination of the radical concentration of the numerator of the assumption was only slightly more successful. It may be seen from equation (23) that the rate of radical formation is quite dependent on which reaction (7,8,9) controls the overall termination process. Dainton, Ivin, and Sheard⁽⁵⁾ found the bi-radical reaction (9) to be the controlling termination reaction in the hexadecene-1-sulfur dioxide copolymerization system. They found $k_{t,SS}$ to be much larger than either of the other termination constants. It is believed that the same type of situation existed in the hexene-1-sulfur dioxide reaction system, namely, $k_{t,HH}$, $k_{t,HS}$, and $k_{t,SS}$ were not equal. If they were not equal, this would have the effect of changing the form of the correlation equations at different initial reactant concentration ratios by changing the radical concentrations for these ratios.

It was also considered quite possible that the concentration conditions were such that other termination reactions involving radical removal by one of the reactant monomers were present in the high hexene concentration reactions. These would probably be of the forms:



Reactions of this type would also lead to the higher observed exponent of .75 on the intensity factor, than the value of .5 predicted by the correlation based on the mechanism outlined in reactions (1) through (9).

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