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RADIATION COPOLYMERIZATION OF STYRENE AND SULFUR DIOXIDE

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GLOSSARY OF SYMBOLS

C	molecular complex of styrene + sulfur dioxide
E	activation energy (kcal/mole)
E_i	activation energy for initiation reaction
E_R	activation energy for overall polymerization reaction
$E_{r_1p_1}$	activation energy for the propagation reactions represented by the rate constants in r_1p_1: $= E_{11} + E_{-21} - E_{12} - E_{21}$
$E_{r_3p_3}$	activation energy for the propagation reactions represented by the rate constants in r_3p_3: $= E_{11} + E_{-32} - E_{32} - E_{21}$
f	fraction of polymer soluble in benzene
G_R	free radicals formed per 100 electron volts absorbed
I	radiation intensity or dose rate (rad/min)
K	equilibrium constant for formation of C
k	reaction rate constant
k_i	rate constant for chain initiation
k_p	rate constant for chain propagation
k_t	rate constant for chain termination
$k_{t\ MM}$	k for termination by $M\cdot + M\cdot$
$k_{t\ SM}$	k for termination by $S\cdot + M\cdot$
$k_{t\ SS}$	k for termination by $S\cdot + S\cdot$
k_{11}	k for propagation by $M\cdot + M \rightarrow M\cdot$
k_{12}	k for propagation by $M\cdot + S \rightarrow S\cdot$
k_{-12}	k for depropagation by $S\cdot \rightarrow M\cdot + S$
k_{21}	k for propagation by $S\cdot + M \rightarrow M\cdot'$
k_{-21}	k for depropagation by $M\cdot' \rightarrow S\cdot + M$

k_{31}	k for propagation by $M\cdot' + M \rightarrow M\cdot$
k_{32}	k for propagation by $M\cdot' + S \rightarrow S\cdot'$
k_{-32}	k for depropagation by $S\cdot' \rightarrow M\cdot' + S$
k_{MM}	k for $M\cdot + M \rightarrow M\cdot$ (Barb's mechanism)
k_{MC}	k for $M\cdot + C \rightarrow C\cdot$ (Barb's mechanism)
k_{CM}	k for $C\cdot + M \rightarrow M\cdot$ (Barb's mechanism)
k_{CC}	k for $C\cdot + C \rightarrow C\cdot$ (Barb's mechanism)
k_{SM}	k for $S\cdot + M \rightarrow C\cdot$ (Barb's mechanism)
k_S	k for $S\cdot \rightarrow M\cdot + S$ (Barb's mechanism)
k_C	k for $C\cdot \rightarrow S\cdot + M$ (Barb's mechanism)
M	styrene monomer, $C_6H_5\text{-}CH{=}CH_2$ (or grams of styrene)
M	moles/liter (in Chapter III only)
$M\cdot$	polymer radical ending in $-M-M\cdot$
$M\cdot'$	polymer radical ending in $-M-S-M\cdot$
$[M],[M\cdot],[M\cdot']$	concentration (moles/liter)
n	molar ratio of styrene to sulfur dioxide in polymer
n_o	n calculated on the basis of the fraction of polymer insoluble in benzene
P	"dead" polymer (or grams of polymer)
p_1	k_{-12}/k_{21}
p_2	k_{-21}/k_{11}
p_3	k_{-32}/k_{21}
R_i	rate of initiation
R_t	rate of termination
r_1	k_{11}/k_{12}
r_3	k_{31}/k_{32}

S	sulfur dioxide, SO_2 (or grams of SO_2)
S·	polymer radical ending in -M-M-S·
S·'	polymer radical ending in -S-M-S·
[S],[S·],[S·']	concentration (moles/liter)
S_p	sulfur dioxide in polymer (or grams SO_2 in polymer)
$[S_p]$	moles SO_2 in polymer per liter of reactant solution
T	temperature ($^{\circ}$C or $^{\circ}$K)
T_c	ceiling temperature ($^{\circ}$C)
t	time (minutes)
γ	factor in Equations (66a) and (68a)
ρ	density (grams/cm^3)
PML	Phoenix Memorial Laboratory
PRF	Phoenix Radiation Facility

ABSTRACT

The copolymerization of styrene and sulfur dioxide, initiated by gamma radiation, was studied over a temperature range of -21° to 95°C at a radiation dose rate of about 1400 rad/min. The reaction was carried out without the use of solvents in sealed, heavy wall glass tubes. Reaction rates were determined from the weight and composition of the recovered polymer. The solubility of the polymers in benzene was also determined as well as the heat stability of several selected samples.

The kinetic and composition data were correlated by a free radical mechanism that assumes repulsion toward SO_2 molecules by polymeric SO_2 units in the penultimate position and reversibility of the propagation steps involving formation of styrene—SO_2 bonds.

The most detailed work was done at 0°C with SO_2/styrene molar ratios ranging from 0.03 to 1.1. Almost all of these runs were limited to less than 2% conversion. The rate data at dose rates of $I = 1250$ to 1460 rad/min fit the equation:

$$-\frac{d[SO_2]/dt}{I^{1/2}[\text{styrene}]} = 4.8 \times 10^{-7}(1 + [SO_2]/4.9)\ \text{rad}^{-1/2}\ \text{min}^{-1/2}$$

which is based on a simplified form of the theoretically derived relationship. Over the wide range of 33.4 to 6040 rad/min, however, the rate data are correlated slightly better by $I^{0.45}$, though the difference in exponents has little statistical significance.

A competing ionic reaction yielding polystyrene is shown to occur at 0°C, affecting the polymer composition and rate of styrene conversion but not the rate of SO_2 conversion.

At other temperatures the reactant composition was varied over a narrower range. An Arrhenius plot of the reaction rate of SO_2 shows a change in slope at about 10°C, indicating a predicted change in mechanism. The overall activation energy is 0.6 kcal/mole below 10°C and 3.9 kcal/mole between 10° and 50°C. Above 50°C the slope steadily decreases. The rate of conversion of styrene, however, continues to increase steadily. The same effect is seen in the polymer composition which is shown to be a function both of temperature and reactant composition. The compositions ranged from 14.6% (by weight) sulfur at -21°C to 5.4% at 95°C.

Polymers containing less than 9.0% sulfur were soluble in benzene. Those containing more than 11.0% were insoluble except for partial solubility of those polymers containing polystyrene from the competing ionic reaction.

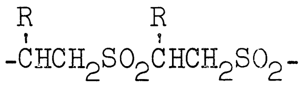
I. INTRODUCTION

A. Literature Survey of Polysulfone Reactions

1. Copolymerization Not Involving Styrene

The first report of a reaction between sulfur dioxide and unsaturated compounds was made by Solonina(93) in 1898. Reacting allyl alcohol and allyl ethers with sulfur dioxide, he obtained amorphous white compounds containing equimolar proportions of sulfur dioxide and allyl monomer with an apparent high molecular weight.

In the 1930's the reaction was investigated extensively by several groups. Seyer and King(89), while determining the physical properties of solutions of hydrogen derivatives of benzene in sulfur dioxide, discovered 1:1 copolymers formed with cyclohexene and cyclohexadiene. Krauze(63) investigated a large number of compounds at room temperature and a few of them at higher temperatures. At the same time, Staudinger and Ritzenthaler(94) studied the reactions of ethylene, propylene and butadiene initiated by peroxide catalysts. They obtained polysulfones with linear, alternating structures for which they proposed a head-to-tail structure:



$$-\overset{R}{\mathrm{C}}\mathrm{HCH_2SO_2}\overset{R}{\mathrm{C}}\mathrm{HCH_2SO_2}-$$

In 1934, C. S. Marvel and his associates began an extensive study of polysulfone reactions.(45, 47, 56, 74, 75, 76, 85, 86, 87) They studied a number of olefins and acetylenes, finding 1:1 copolymers in all cases except for vinyl chloride and vinyl bromide polysulfones for which 2:1 vinyl halide to sulfur dioxide ratios were obtained. The authors investigated the structure of several of the polymers and proposed head-to-head, tail-to-tail structures except for the vinyl halide polysulfones for which a head-to-tail structure was indicated. In a much later paper, Marvel and Weil(76) re-examined the earlier structural evidence and showed that the head-to-tail structure proposed by Staudinger and Ritzenthaler was correct.

The "ceiling temperature" phenomenon was first described in 1938 by Snow and Frey(91) who found that isobutene would not react with sulfur dioxide unless it was cooled below 4°C. In a later paper(92) they described the phenomenon in greater detail and determined the ceiling temperatures for polysulfone reactions of propene, isobutene, 1-butene and 2-butene.

Kharasch _et_ _al_.(61,62) were able to vary the chain length of 1-octene polysulfones and to react allyl chloride and trimethylethylene with sulfur dioxide. Ryden and Marvel,(86) using a less potent catalyst, had not been able to react trimethylethylene with sulfur dioxide.

Except for the ceiling temperature study by Snow and Frey, this early work was done almost exclusively at room temperature. Thus, several of the unsaturated compounds (such as isobutene) reported as non-reactive by the early workers were later found to react with sulfur dioxide at lower temperatures. Most of the reactions were run with high sulfur dioxide concentrations in sealed, heavy wall glass vials or pressure bottles. The sulfur dioxide was condensed into the cooled tubes after the other reagents had been added. The tubes were then warmed to room temperature for the duration of the reaction period -- hours or days, sometimes(63) even months or years.

Comprehensive reviews of the early work were written by Snow and Frey(91) and by Suter(95).

Dainton and Ivin(33) in 1948 were able to explain the ceiling temperature in terms of reversibility of the propagation reaction and defined it as that temperature at which the rate of depropagation equaled the rate of propagation. They showed that the ceiling temperature was independent of the method of initiation but dependent on reactant concentration. By thermodynamic analysis they showed that, in principle, all polymerization reactions should have a ceiling temperature. For the case of pure styrene they calculated from thermodynamic data that the ceiling temperature should be 300°C and verified this experimentally, finding T_c to be between 300° and 330°C. In two succeeding papers(34,37), the authors discussed the thermodynamics of polymerization in greater detail.

Dainton, Ivin and their associates followed these papers with an intensive study of the kinetics and thermodynamics of selected polysulfone reactions. Sealed glass dilatometers were used to observe the reaction rates. Polysulfones were chosen to permit the experimental study of ceiling temperature phenomena at the conveniently low temperatures characteristic of these reactions. First, 1-butene(35,36) and 2-butene(14,15,31) were studied, the reaction with 2-butene being shown to be accompanied by cis-trans isomerization near the ceiling temperature. Their suggestion that stereoisomeric polysulfones were formed from cis- and trans-2-butene was later disproved by Dainton _et_ _al_.(32) and by Skell _et_ _al_.(90)

Dainton, Ivin and Sheard(39) studied the reaction with 1-hexadecene in chloroform solution while Ivin(59) examined the mechanism by which nitrates act as free radical catalysts in sulfur dioxide solutions and Cook, Dainton and Ivin(27,28) showed the effect of olefin structure on the ceiling temperature of the polysulfone reaction.

Grassie(49), in 1956, reviewed the ceiling temperature phenomenon and in 1958, Dainton and Ivin(38) presented a lengthy discussion of the thermodynamics and kinetics of reversibility in addition polymerization.

Dainton and Ivin's group, from 1957 to 1961, published a series of papers that presented a large body of thermodynamic data on sulfones and polysulfones.(10,17,18,19,20,32,72) Most recently, Hazell and Ivin (51,52) studied relative reactivities of olefine by copolymerizing pairs of olefins with sulfur dioxide to obtain terpolymers.

Several other studies of terpolymerization have been reported, (50,57,58,70,79,84) including one using carbon monoxide as one of the monomers.(69)

Ushakof <u>et</u> <u>al</u>.(114) reacted sulfur dioxide with allyl alcohol and its derivatives.

Crouch <u>et</u> <u>al</u>.(29,30) studied emulsion polymerization as a more economical method of polysulfone production.

Naylor and Anderson(80) investigated the degradation of the lower mono-olefin and butadiene polysulfones and found that only the butadiene deviated from first order kinetics above 200°C.

In the recent patent literature, DeJong(41) reported that the sulfur content of ethylene polysulfones could be controlled by changing the reactant ratios in the vapor phase reaction. Others reported polysulfone reactions with bicyclic compounds.(21,43)

The first report of the use of radiation to initiate a polysulfone reaction was by Lewis(67) who reacted sulfur dioxide with ethylene at about 26°C and 400 psi pressure using 25 krad/hr of gamma radiation.

Dainton et al.(39) used beta radiation in some of their work with 1-hexadecene.

Bray(12) studied the radiation initiated reactions of a number of olefins with sulfur dioxide — ethylene, propylene, 1-butene, 2-butene, isobutene, 1-hexene, 1-decene, 1-dodecene, 1,3-butadiene and cyclopropane. Most of the work was done at equimolar composition at 0°C and at about 50 krad/hr from a cobalt-60 gamma source. The 1-hexene-sulfur dioxide reaction was studied in greater detail, at temperatures from -78° to +46°C and radiation intensities from 3 to 920 krad/hr. The reaction rate at 0°C was proportional to the 0.76 power of the radiation intensity. Almost all of the reactions were run in sealed, heavy wall glass tubes. This work has also been published in condensed form.(13)

Henglein et al.(53) used gamma radiation to form cyclohexene polysulfones.

Jobard(60) studied the gamma ray initiated reaction of sulfur dioxide with 1-butene as well as with a number of other olefins at a dose rate of 8000 rad/hr. The 1-butene reaction was also studied using several chemical catalysts.

Kuri and Yoshimura(65) investigated the radiation initiated reaction of vinyl acetate with sulfur dioxide in both the liquid and solid states. The ceiling temperature was -20°C.

2. Styrene-sulfur Dioxide Copolymerization

The copolymerization of styrene with sulfur dioxide was first reported in 1935 by Staudinger and Ritzenthaler(94) who described the copolymer as an inseparable mixture of polystyrene and the 1:1 polysulfone.

Two years later, Glavis, Ryden and Marvel(47) prepared the copolymer at room temperature from equal volumes of styrene and sulfur dioxide with a catalyst of paraldehyde containing some peroxides. They reported on analysis of 18.64% sulfur (compared to 19.05% for the 1:1 copolymer). No one else has been able to obtain this composition except at -78°C.(5,55) The same group(85) also initiated the reaction with ascaridole, an organic peroxide. Marvel and Glavis(75) presented an approximate freezing point diagram for the styrene-sulfur dioxide system, showing a eutectic at 27 mole % styrene with a freezing point of -88°C.

Dorough and Graves(42) obtained a patent in 1938 on the use of sulfur dioxide as a catalyst for the polymerization of styrene at temperatures of 90° to 115°C. They reported that the sulfur dioxide was not incorporated into the polymer.

In 1951, a patent by Noether and Irany(81) gave a number of examples of styrene polysulfones produced under a variety of conditions. These reactions, run at temperatures of 20° to 60°C with reactant mixtures containing very low concentrations of sulfur dioxide, gave polymers containing considerably more than two moles of styrene per mole of sulfur dioxide. The one reaction run at 0°C from a reactant mixture consisting of 8 moles of sulfur dioxide per mole of styrene gave a polymer containing 1.22 moles of styrene per mole of sulfur dioxide. Other reactions were run in aqueous dispersions and emulsions at temperatures from 30° to 81°C with all of the resulting polymers containing more than 2 moles of styrene per mole of sulfur dioxide. The authors also claimed that sulfur dioxide can serve as a catalyst for styrene polymerization above 85°C without being incorporated in the polymer.

Barb(5,6,7) published the first detailed kinetic study of the styrene polysulfone reaction in 1952-1953. Most of the work was done at 20° and 60°C and at low sulfur dioxide concentrations. The styrene concentration was varied from 1.09 to 8.7 molar at 20°C (1.04 to 8.36 at 60°C) using o-dichloro-benzene, tetralin and di-isobutyl sulfone as diluents. At 20°C and above he found a 2:1 minimum styrene to sulfur dioxide ratio in the polymers and interpreted this in terms of a reaction between styrene and a 1:1 styrene/sulfur dioxide complex. Reaction of complex + complex was assumed to occure only at lower temperatures since only at 0°C and -20°C, were polymer compositions of considerably less than 2:1 styrene/sulfur dioxide obtained. At 20°C with very high sulfur dioxide concentrations and in the absence of free radical catalysts, he found the free radical reaction to occur simultaneously with an ionic reaction which produced polystyrene. The two fractions could be separated by precipitating the polymer in benzene which dissolved the polystyrene but not the polysulfone. In his work at 60°C, Barb examined the role of depropagation and determined the approximate activation energies for the reaction. All of the reactions were initiated either by ultraviolet light or by azo-di-isobutyronitrile. The rates at 20° were determined by measuring the uptake of sulfur dioxide in a constant pressure system. The rates at 60° were determined by this method as well as by gravimetric means.

Barb proposed a mechanism which assumed depropagation of terminal complexyl units, even at low temperatures, due to electrostatic repulsion between SO_2 units. In a fourth paper(8) he discussed other variable composition copolymerization reactions in which this same effect might be expected. Walling(115) showed that the same kinetic features are obtained in equations derived without the assumption of participation of a complex.

In 1960, a group headed by Tokura at the Tohoku University in Japan began publishing a series of papers on polymerization in liquid sulfur dioxide. Most of the work involved cationic polymerization of styrene and its derivatives in which no polysulfone was formed.(3,4,98,99,101,105,108,109) Tokura et al.(100,102,103,104),however, also studied copolymerization of styrene and sulfur dioxide with free radical catalysts. The work was done at 40°, 50° and 60° (mostly at 50°) and at high sulfur dioxide concentrations. The authors stated that all of the copolymers contained a 2:1 ratio of styrene to sulfur dioxide and interpreted this as resulting from the homopolymerization of a 2:1 styrene/SO_2 complex. They also determined the effects on the reaction rates of several solvents and salts.

Matsuda, Iino and Tokura(78) obtained terpolymers of styrene, acrylonitrile and sulfur dioxide and correlated the compositions by assuming the copolymerization of acrylonitrile with a 2:1 styrene/sulfur dioxide complex. They showed that this mechanism correlated the data better than a mechanism not involving a complex. The alternate mechanism, however, did not consider depropagation. In justifying this omission, the authors quoted Dainton and Ivin(33) as reporting a ceiling temperature of over 500°C for the polymerization of styrene in sulfur dioxide. Dainton and

Ivin actually reported a ceiling temperature of between 300° and 330°C for the polymerization of pure styrene. Dainton's group never published a study of the styrene polysulfone reaction.

Matsuda *et al.*(78) also discussed the results of Barb and explained the variable composition of his polymers by assuming that at the low concentrations of sulfur dioxide in his work, the sulfur dioxide was consumed in the early stages of the reaction after which only polystyrene was formed. Barb(6) avoided this possibility, however, by rapidly agitating his samples during polymerization in an atmosphere of sulfur dioxide maintained at a pressure in equilibrium with the desired sulfur dioxide concentration in the reaction mixture.

Tokura *et al.* have also studied the radical polymerization of acrylonitrile in sulfur dioxide(110,111), the radical copolymerization of styrene derivatives with sulfur dioxide(106) and the cationic polymerization of isobutene in sulfur dioxide.(107) In the latter report,(107) the authors found that some water was essential to the initiation of the reaction, which was initiated by a SnCl catalyst. No polymer was formed when water was carefully excluded.

Two papers concerning the radiation initiated copolymerization of styrene and sulfur dioxide have recently been published by Herz, Hummel and Schneider.(54,55) The work covered the temperature range from -78° to +30°C and was limited to high sulfur dioxide concentrations. It is primarily a composition study but includes some rate data at 30°C. The work was done at a dose rate of 8700 rad/min. with a cobalt-60 source. A simultaneous cationic polymerization, yielding polystyrene, was observed, especially at the lower temperatures. The authors found that low concentrations of acetone suppressed this reaction without appreciably affecting the free radical rate. At -78°C, when using acetone to inhibit the cationic reaction, they obtained polymer compositions very close to equimolar in styrene and sulfur dioxide. These polymers were found to have almost identical properties to those of the strictly alternating polymers obtained by the oxidation of poly(styrene sulfide). This method of preparing 1:1 styrene/sulfur dioxide copolymers had been reported earlier by Noshay and Price.(82)

Several recent reviews are available: Bray(12) reviewed the literature on polysulfone reactions to 1956 with a particularly complete coverage of the earlier work. Dawans and Lefebvre(40) published a review of polysulfones covering the literature to 1960 and emphasizing both the American and European patent literature. Magat(73) reviewed the work in radiation initiated ionic polymerization. Charlesby(24) and Chapiro(22) have written review books on radiation polymerization and radiation effects in polymers. Chapiro emphasized polymerization reactions more than did Charlesby who concentrated on the irradiation of polymer systems. Swallow(96) wrote a more general review on the radiation chemistry of organic compounds which includes sections on polymerization and polymers.

B. Theory

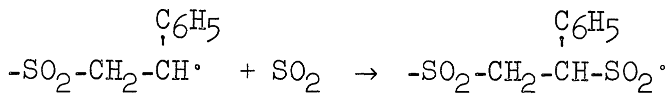
1. Polysulfone Reactions

a. General Features of the Reaction

The usual copolymerization is a free radical reaction involving two monomers, each able to react with itself or the other. Thus, by varying their relative concentrations, a full range of polymer composition is possible. When sulfur dioxide is used as one of the monomers, however, the situation changes. Since this compound will not react with itself, copolymers containing it can have a maximum of only 50 mole percent sulfur dioxide.

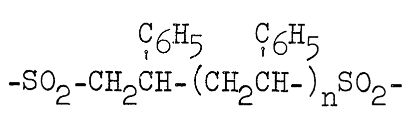
Most of the polysulfone reactions that have been studied thus far have, in addition, involved olefins that, under the conditions of the reaction, have such a low rate of homopolymerization, that only olefin-sulfur dioxide reactions occur so that only strictly alternating copolymers are formed.

Styrene, with its particularly reactive double bond, is able to react readily with itself yielding copolymers containing, in all cases, more than one mole of styrene per mole of sulfur dioxide. Barb(6,8) has shown also that a sulfur dioxide unit in the penultimate position in the polymer radical exerts a strong repelling effect on a SO_2 molecule so that the reaction



$$-SO_2-CH_2-\overset{C_6H_5}{CH}\cdot + SO_2 \rightarrow -SO_2-CH_2-\overset{C_6H_5}{CH}-SO_2\cdot$$

does not readily occur, even at low temperatures, and at higher temperatures (above about 20°C) only structures of the type



$$-SO_2-CH_2\overset{C_6H_5}{CH}-(CH_2\overset{C_6H_5}{CH}-)_nSO_2-$$

are formed, where $n \geq 1$. Walling(115) has interpreted these observations in terms of a highly reversible reaction step between sulfur dioxide and the styrene radical. Barb,(5) earlier proposed an equivalent scheme involving the reaction between styrene and a 1:1 styrene-sulfur dioxide complex which he showed to exist in low concentrations. Dainton, Ivin and their associates had postulated a similar mechanism (involving the homopolymerization of 1:1 olefin-sulfur dioxide complexes) to explain the copolymerization between sulfur dioxide and the olefins they studied. However, in the latest paper to come from this group, Hazell and Ivin(52) conclude that they have been unable to differentiate between this mechanism and one involving separate reversible additions of olefin and sulfur dioxide with one of the steps being highly reversible.

b. Depropagation - the "Ceiling Temperature"

Addition polymerization is an exothermic process and involves a decrease in entropy. An increase in temperature is therefore thermodynamically unfavorable to the reaction, and whatever the particular reaction mechanism, a temperature will be reached where the reverse reaction will predominate. At the ceiling temperature (T_c), propagation and depropagation are in equilibrium and

$$\Delta F = \Delta H_p - T\Delta S_p = 0 \qquad \text{(a)}$$

or

$$T_c = \Delta H_p / \Delta S_p \qquad \text{(b)}$$

where ΔH_p and ΔS_p are the enthalpy and entropy changes for the propagation step under the prevailing experimental conditions.

For the simple case of a free radical polymerization involving only one monomer (M), the propagation rate (R_p) is given by

$$R_p = (k_p[M] - k_d)\ [M\cdot] \tag{c}$$

where k_p and k_d are the rate constants for propagation and depropagation and $[M\cdot]$ is the free radical concentration. At T_c the net reaction rate is zero and if the rate constants are expressed by the Arrhenius relationship:

$$k_p = A_p \exp(-E_p/RT) \quad \text{and} \quad k_d = A_d \exp(-E_d/RT) \ ,$$

Equation (c) becomes

$$A_p \exp(-E_p/RT_c)\ [M] = A_d \exp(-E_d/RT_c)$$

which gives

$$T_c = \frac{\Delta H_p}{R \ln (A_p[M]/A_d)}$$

where $\Delta H_p = E_p - E_d$. Since from transition state theory $A = (kT/h) \exp(\Delta S^*/R)$ (where k is the Boltzmann constant, h is Planck's constant, and ΔS^* is the entropy of activation) we obtain

$$T_c = \frac{\Delta H_p}{S_p^o + R \ln [M]} \tag{d}$$

where $\Delta S_p^o = \Delta S_p^* - \Delta S_d^*$ is the standard entropy change for unit concentration. Equation (c) will not hold very close to T_c since k_p and k_d are no longer independent of the polymer chain length when the chain is very short as it is close to the ceiling temperature.

Dainton and Ivin(38) in their more complete discussion of this topic also state that the existence of the ceiling temperature "is a direct result of the fact that polymerization is a chemical aggregation process. A similar and more familiar situation exists for physical aggregation processes: thus a solid cannot be obtained from a liquid unless the temperature is below the freezing point of the liquid. Solid, liquid, and freezing point are physical analogs of polymer, monomer and ceiling temperature".

In the case of the usual polysulfone reaction involving only reaction of monomer (M) with sulfur dioxide (S), Equation (d) becomes

$$T_c = \frac{\Delta H_p}{\Delta S_p^o + R \ln [M] [S]} \qquad (e)$$

In the styrene polysulfone reaction, however, the situation is more complex since styrene reacts with itself as well as with sulfur dioxide.

Ceiling temperatures for polysulfone reaction are much lower than those for vinyl polymerizations since the carbon-sulfur bond is weaker than the carbon-carbon bond. With styrene polysulfone we have in effect two ceiling temperatures, one involving depropagation of styrene-styrene bonds and the other involving styrene-sulfur dioxide bonds. Since the reaction temperatures are far below the ceiling temperature for styrene polymerization (about 300°C), the polymer chain can depropagate only until a styrene-styrene bond is reached. Therefore, instead of a steady reduction in reaction rate as the ceiling temperature is approached, the rate continues to increase but the sulfur dioxide concentration in the polymer decreases until, at a high enough temperature, only polystyrene is formed.

More detailed discussions have been written by Dainton and Ivin,(33,37,38) Grassie,(49) Laidler,(66) and Walling.(116)

c. Ionic Polymerization as a Side Reaction

Styrene polymerizes readily at low temperatures by a cationic mechanism and Tokura *et al.*(109) have shown that sulfur dioxide is an excellent solvent in which to conduct the reaction. This reaction has a negative temperature coefficient and occurs rapidly at very low temperatures, but Barb(5) has shown that even at 20°C, the reaction will occur at high SO_2 concentration. Polysulfones are not formed by this mechanism; only polystyrene results.

Free radical polymerization is characterized by mutual termination since radicals usually have very high reactivity with other radicals. This mode of termination results in a reaction rate that is proportional to the square root of the initiation rate. Mutual termination, however, is unlikely in ionic polymerization because of repulsion between two active centers carrying like charges. Accordingly, ionic reactions are usually characterized by rates proportional to the rate of initiation.

2. Definitions of Radiological Units

Rad - The unit of absorbed dose. One rad is equal to 100 ergs/gram of energy imparted to any substance by ionizing radiation. Many of the earlier values of absorbed dose were based on the obsolete unit rep (roentgen-equivalent-physical) which was usually, but not always defined as the absorption of 93 ergs per gram.

Roentgen - The unit of "exposure" dose. One roentgen is an exposure dose of X- or gamma radiation such that the associated electron emission per cubic centimeter of dry air at STP (0.001293 grams) produces, in air, ions carrying 1 esu of electric charge of either sign. This is equivalent to the absorption of 88 ergs per gram of air.

Curie - One curie is the amount of radioactive material which decays at the rate of 3.700 x 10^{10} disintegrations per second.

LET - Linear energy transfer rate.

G - The G value is a convenient way of expressing chemical yield. G_X is the number of chemical events of type X occurring per 100 ev of absorbed energy. G_R is the number of free radicals formed per 100 ev.

3. Radiation Polymerization

a. Interaction of Gamma Radiation with Matter

Cobalt-60, the most widely used source of γ-rays, produces photons of 1.17 and 1.33 Mev and β-particles of 1.48 Mev maximum energy. The β's are completely absorbed by 1/32 inch of steel so the usual stainless steel encapsulated cobalt-60 source is essentially only a gamma source.

Absorption of these energetic γ-rays by elements of low atomic number is almost exclusively by Compton scattering although photoelectric absorption may be important if enough mass is between the source and the sample to appreciably degrade the energy spectrum. Compton scattering is an elastic collision between a photon and a single electron; the incident photon gives up a portion of its energy to the electron and a photon of lower energy is emitted. The energies of the Compton electrons are dependent on the energy of the incident photon and its angle of deflection and therefore a continuous energy spectrum is obtained with a mean of about 0.5 Mev from Co^{60} gammas. It should be noted that Compton electrons also enter the sample from γ-radiation absorbed in the wall of its vessel thereby increasing the radiation intensity within a millimeter or two of the wall.

Most of the chemical effects are produced from the stopping of these high energy electrons rather than from the original γ-rays. These fast electrons lose energy almost entirely by electrostatic interaction with the electrons of the absorbing medium. The initial result is, therefore, the production of several thousand cations, free electrons and excited molecules per Compton electron.

These primary species can undergo secondary reactions:

(1) The electrons can recombine with the positive ions producing additional excited molecules. Slow electrons can also combine with molecules having high election affinity to form negative ions. In addition, electrons with sufficient kinetic energy can act the same as the original Compton elections.

(2) Positive ions can undergo very rapid recombination with thermal electrons producing excited molecules with considerably higher energy levels than are produced by direct interaction with fast electrons. These cations can, of course, also neutralize anions if they are present.

(3) Excited molecules can dissociate into molecular products or transfer their excitation energy to other molecules. However, their most important reaction is dissociation into free radicals.

b. Special Features of Radiation Polymerization

The free radicals and ions resulting from the absorption of radiation can initiate polymerization by much the same mechanisms experienced with chemical catalysts or ultraviolet light. The early work led to the belief that ionic polymerization could not be initiated by ionizing radiation, but later studies showed that cationic and anionic mechanisms would proceed under proper conditions. Free radical mechanisms, however, have been shown to account for most of the experimental results now available.(22)

Radiation induced free radical polymerization has several special features:

(1) Radical initiation is not a function of temperature (i.e., $E_i = 0$), thereby reducing the overall activation energy for the reaction. This situation may not hold true at very high initiation rates due to termination by primary radicals.

(2) Since ample energy is available to break the polymer chains, initiation can also result from polymeric radicals. This situation can increase the molecular weight of the polymer and, in some systems, cause cross linking. A change in the initiation rate with polymer concentration can also result. The rapidly growing study of graft polymerization is largely a result of this phenomenon.

(3) Inert solvents do not exist in radiation polymerization. The best that can be hoped for is to find a solvent that has a fortunate combination of properties so that it acts like an inert solvent. It should, in particular, have the same G_R value as the monomer and produce similar types of radicals. The solvent should, in addition, lead to minimum energy transfer and chain transfer reactions.

(4) At high dose rates it can no longer be assumed that the primary radicals are not involved in termination reactions with polymer chain radicals or other primary radicals. As a result, the polymerization rate will be proportional to less than the square root of the dose rate.

(5) At dose rates low enough so that the free radical clusters (generated by the slowing down of the fast electrons) do not overlap, each cluster can be considered an isolated system. In this case, all chains started in a cluster, are terminated by radicals from the same cluster and the overall rate of polymerization will be directly proportional to the dose rate. The required dose rates of gamma radiation for this effect to be seen is so low that it can probably be seen only with radiation of very high LET such as alpha particles. Kupperman(64) presented a diffusion kinetic model to interpret this type of phenomenon.

(6) Radiation can initiate both free radical and ionic mechanisms in the same system. For styrene, Chapiro and Stannett(23) have shown that in 1,1,-dichloroethane the mechanism changes from free radical to cationic simply by reducing the temperature. Chen and Stamm(25) have obtained similar results with methylene chloride as a solvent as has Chen(26) with undiluted styrene. In addition, Tsuda(112,113) has shown that, at -78°C, the predominant mechanism for the copolymerization of styrene and acrylonitrile can be changed from cationic to anionic by changing solvents from methylene chloride to dimethyl formamide, toluene, diethylamine or ethyl bromide. In bulk, free radical copolymerization predominated.

More detailed explanation of these topics may be found in reviews by Chapiro,(23) Charlesby,(24) Allen,(1) Lind,(68) and Laidler.(66)

II RADIATION SOURCES

Both the 1600 curie and the 2700 curie (as of January 1963) cobalt-60 sources at the University of Michigan were used in this study. Almost all of the work was done with the 1600 curie source at the Phoenix Radiation Facility (PRF) which was formerly the Fission Products Laboratory. The 2700 curie source at the Phoenix Memorial Laboratory (PML) was used for the high intensity runs since it has a maximum dose rate of about five times that of the PRF source.

The PRF source consists of 42 aluminum clad rods, 10 in. x 3/8 in. diameter with about 40 curies of Co^{60} in each. It is located in a cave shielded by 4 ft. concrete walls and is mounted on an elevator which can lower the source into a water filled well when it is not in use. The elevator is powered by a hand cranked mechanism which has proved to be fast and reliable, but not effortless.

In 1959, this source was found to be leaking and a generally poor condition as far as the aluminum cladding was concerned.(83) It was therefore reencapsulated, in 1960, in a single annular stainless steel container which was designed so that it would be loaded under water, sealed, dried and kept pressurized with nitrogen.(83) This system has remained leak tight in three years of use. Figure II-1 shows a photograph of the assumbled container before the outer shell was welded on. The rods were loaded through the single opening in the top of the annulus with the turntable being totated, after each insertion, to bring an empty hole in

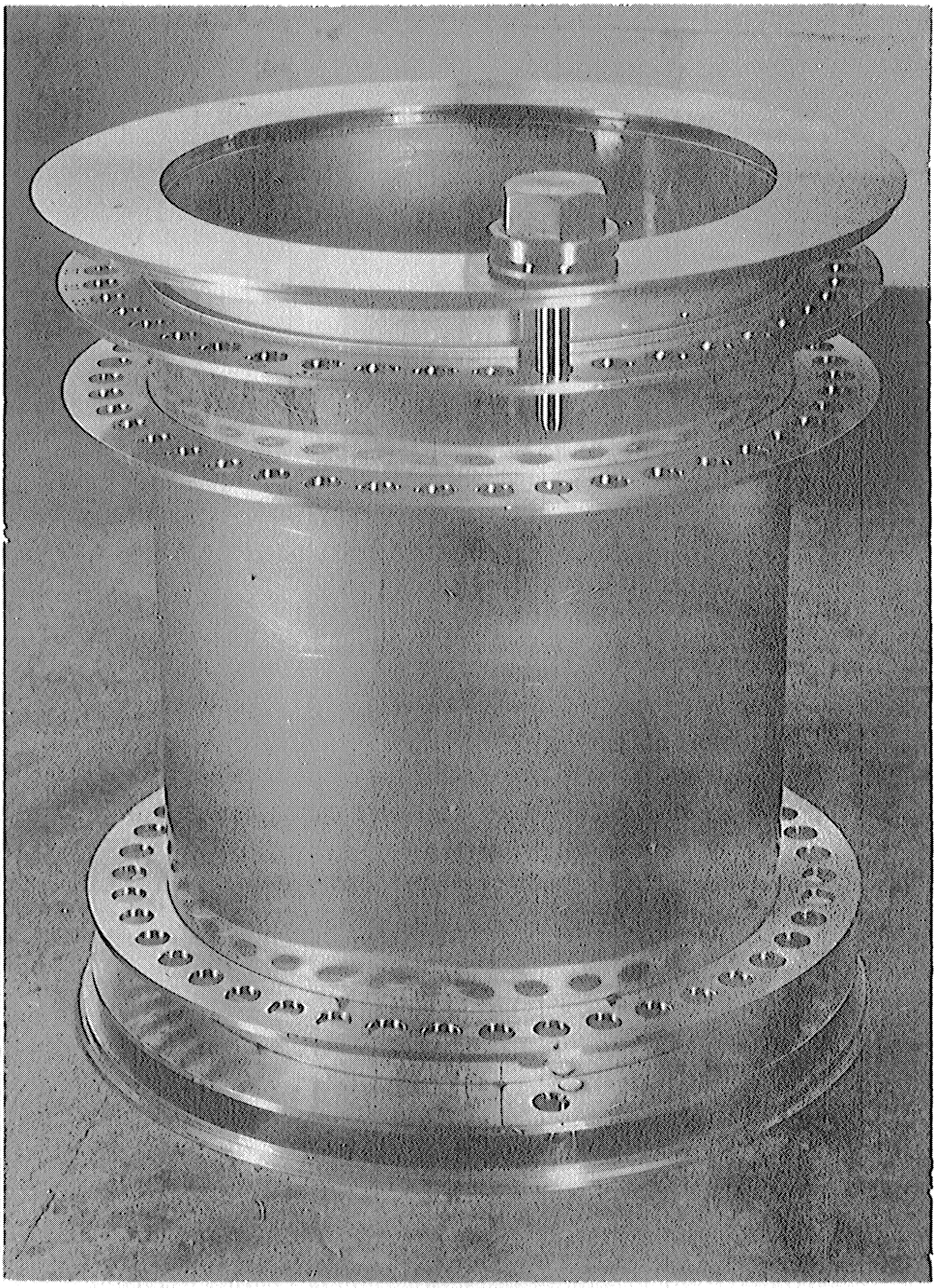


Figure II-1. Interior of PRF Cobalt-60 Source Container Before Welding on Outer Shell.

place. The forty third hole which is occupied by the locking pin on the plug is in the southwest direction and results in a very slight reduction in dose rate adjacent to that position.

When the source is raised, it enters a perforated stainless steel basket which has the dual function of protecting the freedom of movement of the source and aiding in the placement of experimental objects to be irradiated. It surrounds but does not touch the source container when the source is in the elevated position. The center well of the basket extends through the center of the annular source container and is 17.8 cm in diameter and 30 cm deep. Figure II-2 shows the basket with the two elevator rods. The steel platform conceals an emergency release mechanism which can drop the basket into the well in case the source should jam inside.

The radiation field in this center well has recently been mapped by J. T. Graikoski and N. C. Kothary.(48) Figure II-3 shows their map with a typical reaction tube superimposed in its correct position showing the approximate dose distribution within the tube.

The PML source consists of 350 aluminum slugs 1-1/8 in. x 3/8 in. diameter which are contained in 35 aluminum tubes, 10 slugs per tube, and held in place by pins at the top and bottom. The much higher dose rate available with this source is due primarily to the tighter configuration; the center well is only 7.5 cm in diameter and 33 cm deep. This source is also located in a shielded cave and is lowered into its well by an electrically driven elevator.

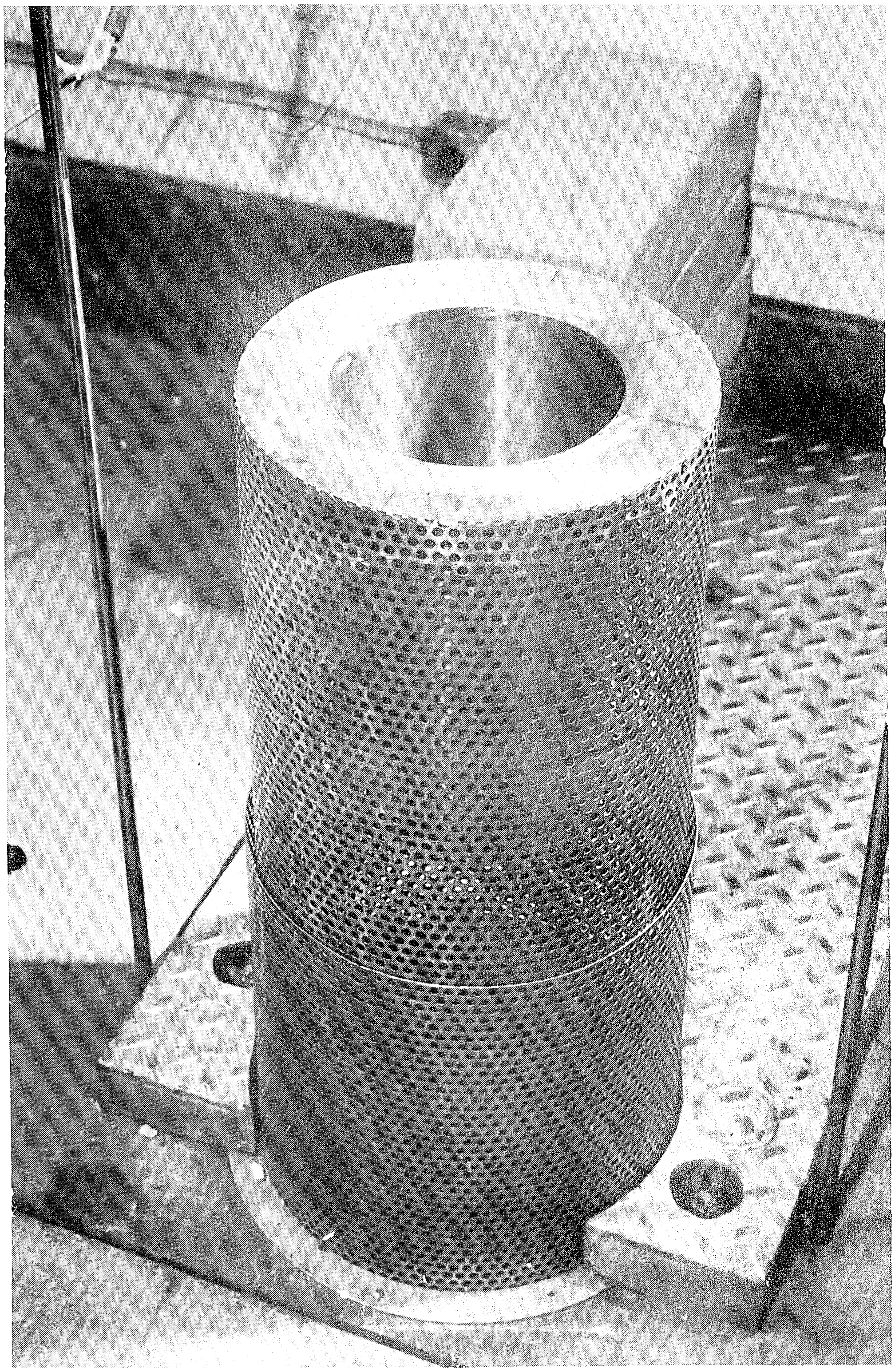


Figure II-2. Basket for PRF Cobalt-60 Source.

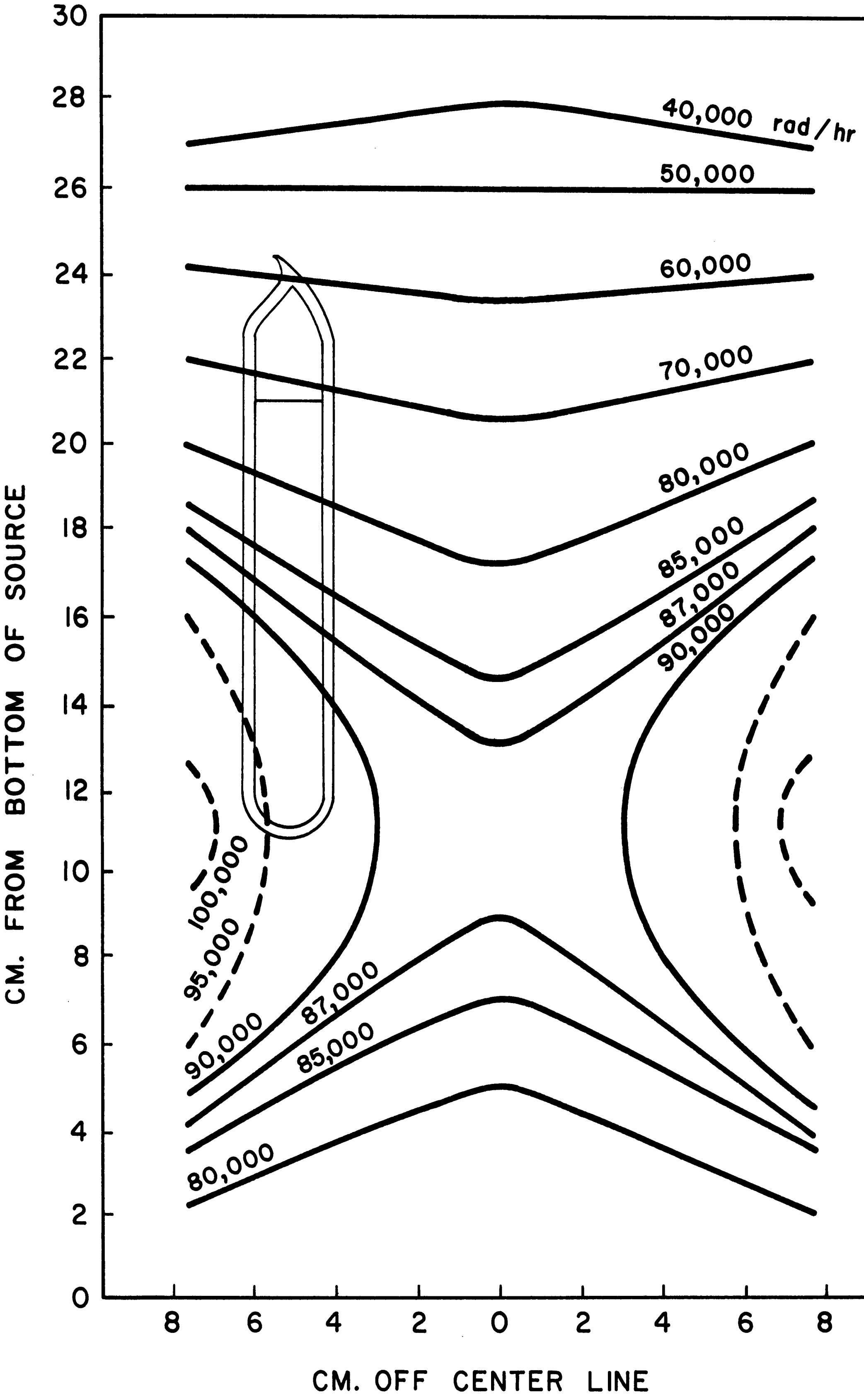


Figure II-3. Map of Radiation Field in Center Well of PRF Source Basket.(48) Position of Reaction Tube is Shown.

III EXPERIMENTAL PROCEDURE

A. Reagents

1. Sulfur Dioxide

Matheson anhydrous sulfur dioxide from a single No. 2 cylinder (Cyl. No. M-7193) was used for all experiments. The gas was stated to have a purity of 99.8% with 0.0012% water and 0.2% non-condensable gases, and was used without any further purification.

2. Styrene

All the styrene used in the work was Eastman No. 1465 which is stabilized with tert-butylpyrocatechol. It was supplied in one kilogram bottles which were kept in a freezer until used.

The styrene was purified by vacuum distillation at about 60 mm mercury pressure, corresponding to 70°C at the top of the column. Matheson prepurified nitrogen was bled into the system to maintain the desired pressure. Severe bumping was a problem at first. Boiling chips did not help but bubbling some of the nitrogen into the bottom of the still and maintaining a pressure not much lower than 60 mm mercury were effective in controlling it. Para-xylene was used as a substitute for styrene in working out some of the problems of operation of the still. (Ortho-xylene would have been a better substitute since its vapor pressure is within 1°C of that of styrene from below 40 mm to over 760 mm mercury pressure, but it was not in stock at the Chemistry Store at the time).

The final form of the still is shown in Figure III-1a and was used in all runs after No. 221. The vacuum jacketed distillation column was 30 cm long, 19 mm ID, and packed to a depth of 28 cm with 1/8 in. ID glass helices. Liquid holdup at the inlet joint of the Friedricks condenser was avoided by removing the joint and fusing the condenser and the adaptor tube at the top of the column into a single unit. The only place where it was not possible to avoid contact of the distilled styrene with a lubricated joint was at the stopcock on the distillate receiver. Lubrication of this Teflon plug stopcock was necessary for vacuum tightness. To minimize contamination, a hydrocarbon insoluble grease, Nonaq (Fisher Scientific Company), was used.

The condenser, distillate receiver, and the one liter product flask into which it drained, were wrapped with aluminum foil to eliminate any possible effects of exposure to light during the approximately three hours required for the distillation. The product flask, in addition, was kept packed in crushed ice. Figure III-1b shows the still as set up for operation.

For most of the work, a full bottle (1 kg) of styrene was distilled at a time, yielding enough distillate to fill 25 reaction tubes with 20 ml of styrene in each.

Operation of the Still -- (Refer to Figure III-2) Before starting to heat the charge of styrene, the system was evacuated and maintained at about 20 mm mercury pressure by bubbling nitrogen into the distillation flask. After about 10 minutes the heating mantle was

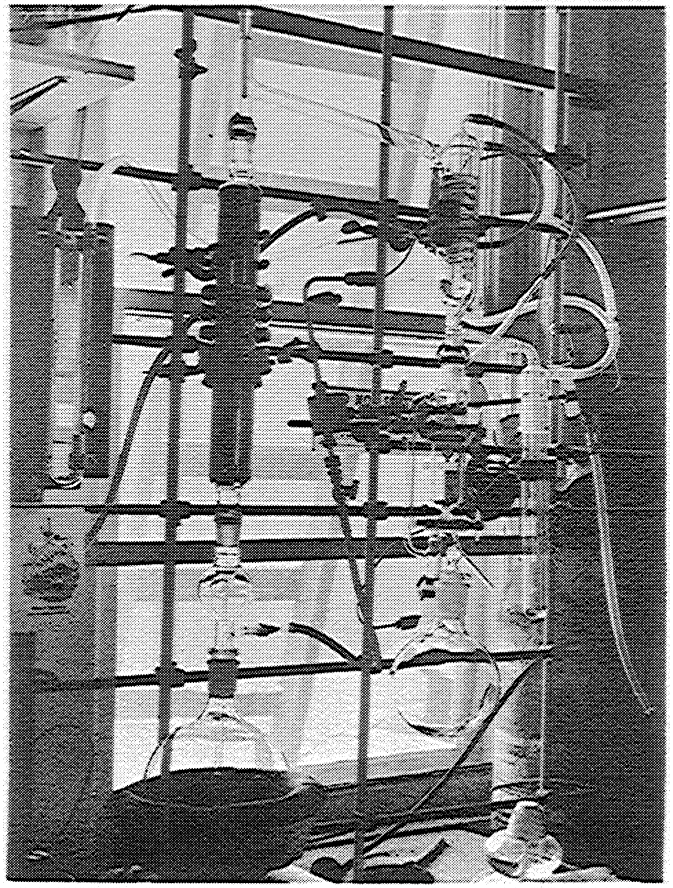


Figure III-1a. Vacuum Distillation Unit for Styrene Purification.

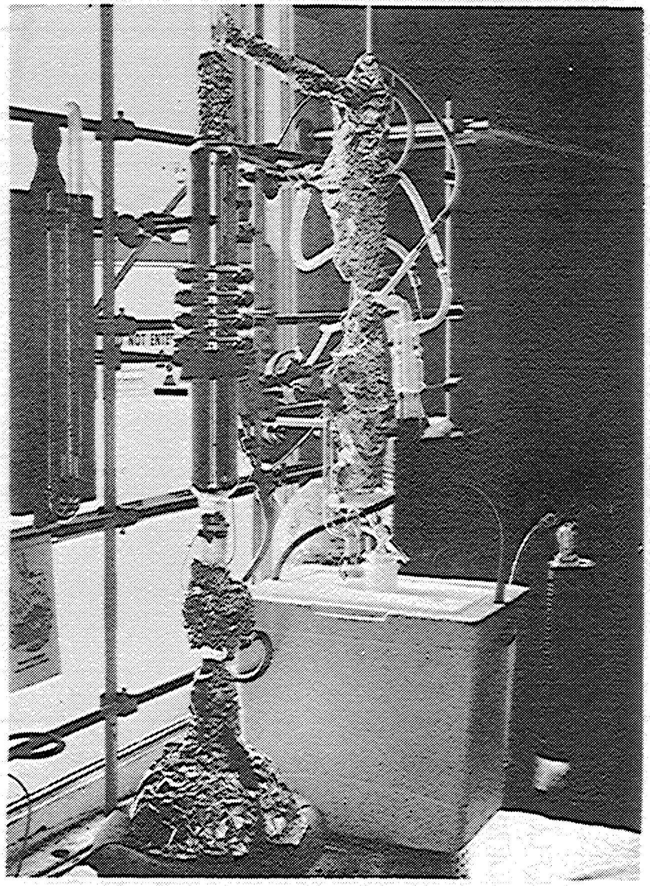


Figure III-1b. Unit as it Appears in Operation.

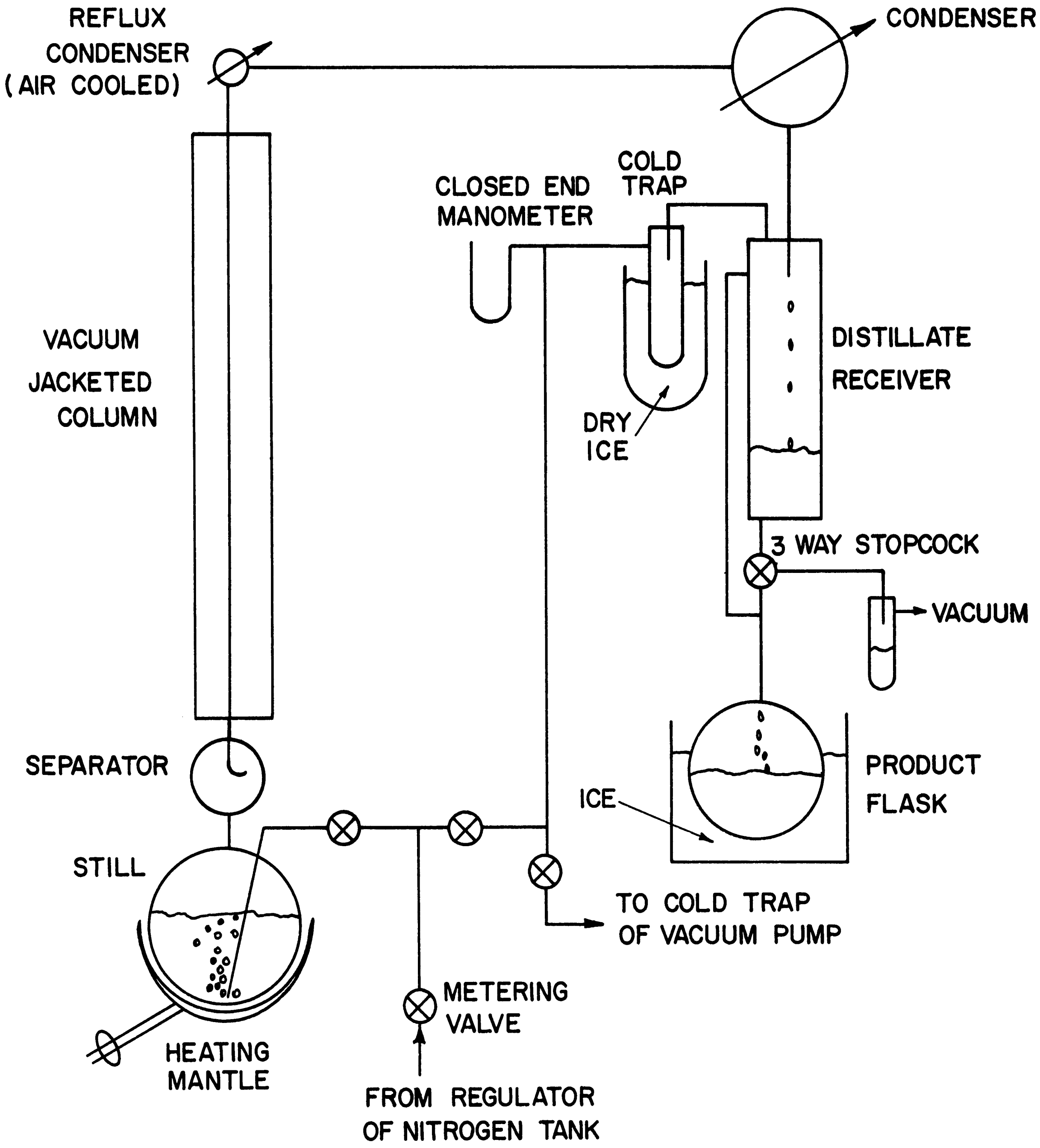


Figure III-2. Schematic Diagram of Vacuum Distillation Unit.

turned on and the vacuum valve partially closed to raise the pressure to 60 mm. Since more nitrogen was required to maintain the pressure than was needed to prevent bumping in the still, only a portion of the gas stream was introduced into the still. The overall nitrogen flow was controlled by a metering type needle valve with a finely tapered stem. Use of this valve permitted accurate pressure control without difficulty. With a 2 liter round bottom flask, the Glas-Col heating mantle was operated at 45 to 46 volts, resulting in an output of about 4 to 5 ml of distillate per minute with a reflux ratio between 1.1 and 1.4. The reflux ratio was measured by counting drops at the bottom of the column and at the inlet to the receiver and is therefore only approximate. To regulate the reflux, the adaptor tube on top of the column was converted into an air condenser by directing a stream of compressed air against it.

The first 200 ml of distillate were discarded. In order to remove this liquid without breaking the vacuum on the system, a three way stopcock was used on the distillate receiver. A glass tube (a spare cold trap) was connected with a short length of Tygon tubing to the side arm of the stopcock; the tube was evacuated and the stopcock slightly opened. This operation was repeated three or four times to minimize the quantity of the initial distillate remaining on the wall of the receiver. The stopcock was then turned to drain to the product flask and left this way for the remainder of the distillation.

When 600 ml of distillate product had been collected, the distillation was stopped. By this time, due to polymerization, the remaining styrene in the still was rather viscous. This could have been avoided by the addition of additional inhibitor but the polymerization was not troublesome. The system was carefully brought to atmospheric pressure by closing the vacuum valve and increasing the nitrogen flow. The product flask was kept under nitrogen until the styrene was transferred to the reaction tubes.

The reaction tubes (described in part B) were filled by shiponing directly from the product flask into the tubes (see Figure III-3a). The styrene was first warmed to room temperature to avoid water condensation. Then the stopper was removed from the center neck of the flask (a two necked flask was used) and a glass siphon with a replaceable outlet tube of 3 mm glass tubing which would fit through the neck of the reaction tubes. With the flask under slight nitrogen pressure (controlled by a slit valve cut in a piece of rubber tubing) each of the reaction tubes was filled with 20 ml of styrene. (The tubes before No. 132 were filled with 15 ml of styrene.)

The tubes had previously been calibrated by filling with 20 ml of water from a hypodermic syringe fitted with a 6 inch neddle. The level was marked with a titanium tipped glass marking pencil which leaves an adherent deposit of titanium that is not removed in the cleaning process. This method of marking is preferable to scratching the glass since, when the tubes are used under pressure, they may crack at a scratched mark.

Immediately after filling, the tubes were sealed with rubber serum caps and evacuated through hypodermic needles inserted through them (see Figure III-3b). While on the vacuum pump, the tubes were placed in a dry ice

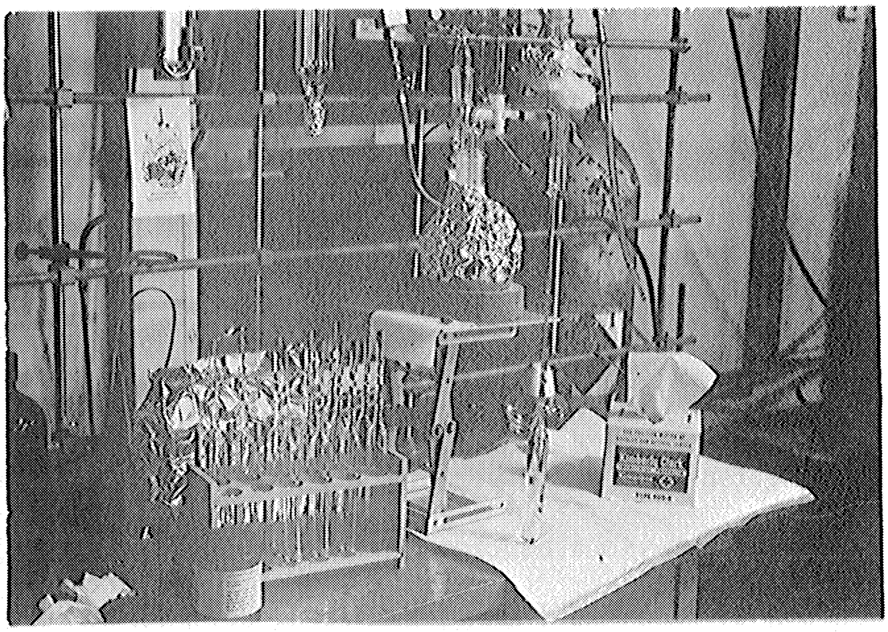


Figure III-3a. Loading Reaction Tubes With Styrene by Means of Syphon.

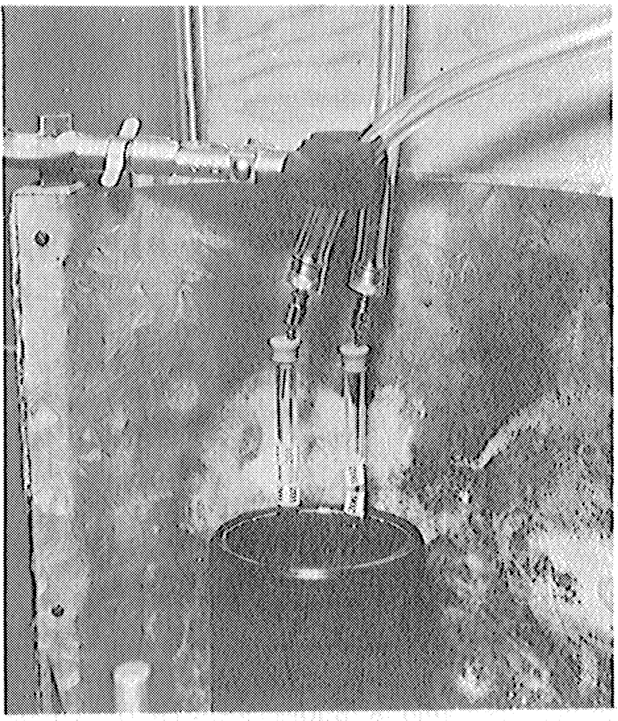


Figure III-3b. Degassing Styrene Filled Tubes.

slush bath and frozen. After being rewarmed for weighing on a Torsion balance, they were stored in dry ice in a 10 liter dewar flask until ready for use.

B. Reaction Equipment

1. Reaction Tubes

Heavy wall Pyrex glass tubes similar to those used by Bray(12) were used for all runs. The tubes were made to specification from 1 in. OD tubing by the glass blowing shop of the Chemistry Department. The constriction at the top permits easy sealing while under vacuum. As noted in the previous section the constriction was specified to be large enough to pass the 3 mm glass tubing used for loading the vials with styrene. The full specifications for the tubes are given in Figure III-4. The 6-1/2 inch maximum length permits the sealed, loaded tubes to fit upright on the pan of the analytical balance for easy weighing. In order to facilitate cleaning, the extension above the constriction was limited to 4 inches in length.

The tubes were cleaned by filling with sulfuric acid-sodium dichromate cleaning solution and holding overnight at 70°C. The solution was drained by inverting the tube into a suction flask connected to a water aspirator. For final rinsing, an arrangement was used which permitted a vigorous flow of water with its simultaneous removal by suction. To do this, the arms of the straight part of a glass T tube were cut as short as possible. One side was sealed with a rubber serum cap and a short length of rubber tubing was slipped over the opposite arm. A 6 inch, 20 gage hypodermic needle was forced

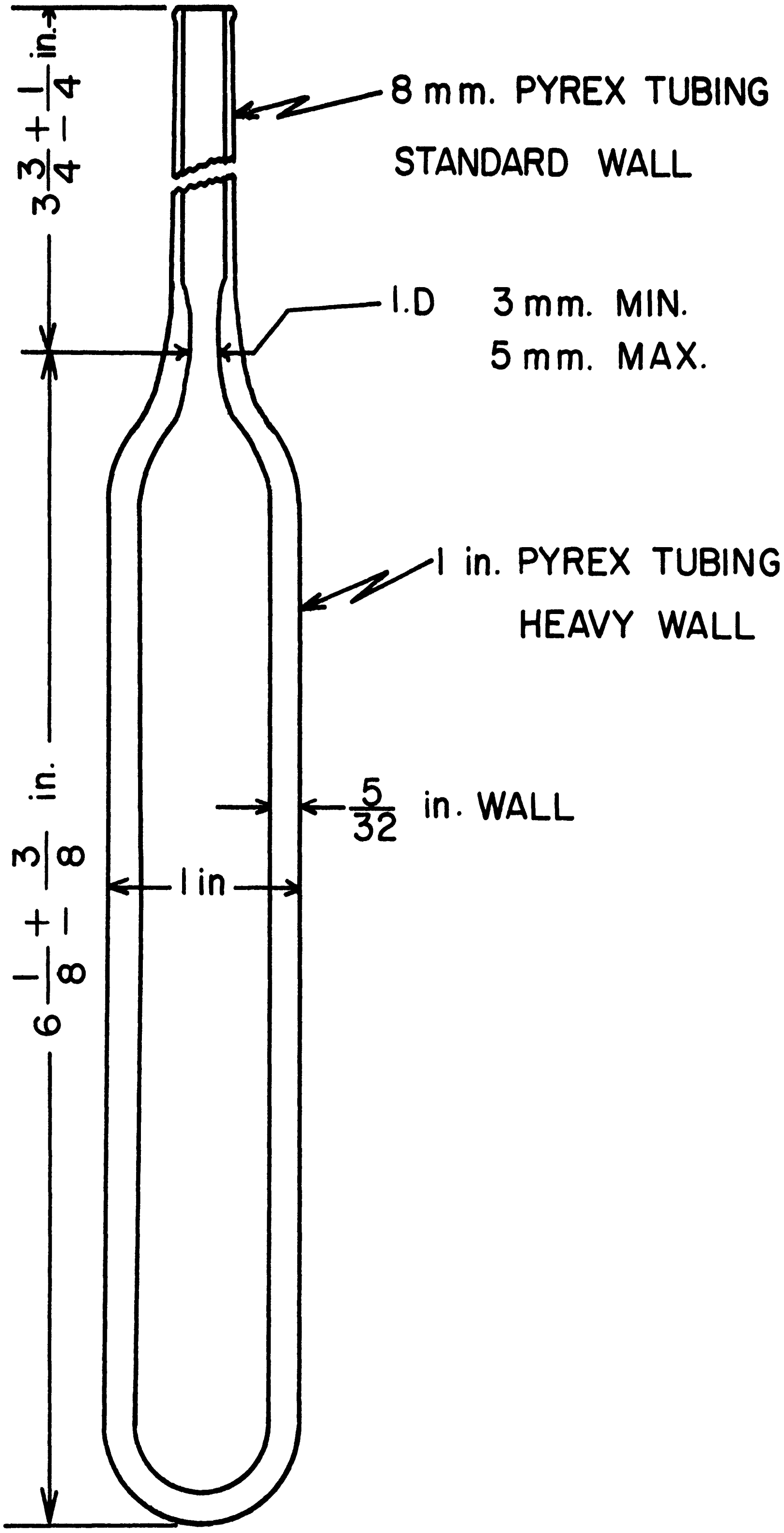


Figure III-4. Specifications for Reaction Tubes.

through the serum cap so that its point extended at least 4 inches past the opposite arm. With the needle connected to the distilled water tank, the side arm connected to an aspirator, and a reaction tube connected to the rubber tubing a rapid flow of water over the inner surface of the reaction tube was obtained with a minimum waste of water. A brief rinse with double distilled water completed the washing procedure. The tubes were inverted in a 110°C oven to dry and then sealed with rubber serum caps or aluminum foil until ready to use.

2. Temperature Control Methods

All irradiations were performed in glass dewar flasks. The significant dimensions of the three flask sizes which were used are as follows:

Dewar	Overall Height mm	I.D. mm	O.D. mm	Bottom of Tubes To Base of Dewar mm
2 liter (A)	275	122	155	105
2 liter (B)	266	118	150	111
400 ml	285	44	69	32

Dewar (A) was broken after run No. 153 and was replaced by dewar (B). Corrections were made for the differences in dose rate resulting from the slightly different dimensions of the two flasks. The 2 liter dewars were used for all runs conducted in the center well of the PRF Co-60 source. The 400 ml flask was used in the smaller, higher radiation intensity center well of the PML Co-60 source and the low intensity runs outside of the center well of the PRF source.

At temperatures below 0°C, eutectic mixtures of salts and ice were used for temperature control. Two such mixtures were used. A 20% KCl mixture gave a temperature of -10°C and a 24% NaCl mixture gave -21°C. The ice was used in the form of freshly fallen snow which was stored in a freezer. The salts were also kept in the freezer and were mixed with the snow while below the eutectic temperature. In this way, little or no liquid was formed until the mixing was completed enabling a uniform mixture to be easily obtained. The use of snow avoided the trouble of pulverizing ice and the problem of separation of components when crushed ice is used without being pulverized.

At 0°C, crushed ice was used to maintain the temperature with just enough water to fill the voids between the ice particles. Between 10°C and 30°C, the insulating ability of the dewar flask was relied on to maintain the constant temperatures which could be held within 1°C over the time of the irradiation. This method was attempted for higher temperatures but was not successful. Its usefulness is also limited to moderate doses since 1 megarad is the equivalent of 2.4 cal/gm.

At temperatures above 30°C an electrically heated rod-shaped heater was used. A Leeds and Northrup Model 10769-G temperature controller regulated the water bath temperature by means of a copper-constantan thermocouple. Temperature gradients were reduced by agitating the bath with an electrically driven stirrer. Since the reaction tubes occupied the periphery of the flask and the heater was in the center, the only place left for the propeller of the stirrer was in the unoccupied space at the very bottom of the dewar flask. A perforated aluminum disk, on which rested the tubes and the heater, prevented obstruction of the stirrer which spun below the disk. The tubes were held against the wall of the dewar by a wire mesh cylinder attached to this bottom plate. The assembled system in place in the center well of the Co-60 source is shown in Figure III-5. In order to prevent the flask from shifting from the vibration of the stirrer it was wrapped with 1/2 inch of plastic foam which insured a snug fit in the well.

C. Reaction Procedure

1. Sulfur Dioxide Loading

The reaction tubes were loaded with sulfur dioxide immediately before irradiation. As a result of the experience gained from the first couple of dozen runs it was determined that the required level of condensed sulfur dioxide in the tube could be estimated by allowing 2.2 mm of tube height per gram of SO_2 and starting the measurement from a level 10 mm below the mark corresponding to the level of styrene at room temperature. Upon removing the styrene filled tubes from the dry ice storage dewar this new level was marked on the tubes. The titanium glass marker worked particularly well on the cold, frost covered glass.

The sulfur dioxide was condensed into the tubes on the vacuum manifold, shown in Figure III-6, which provides for the evacuation and loading of one to three tubes at a time. The vacuum pump (Welch, Model 1405) was connected to the stopcock at the far left and the

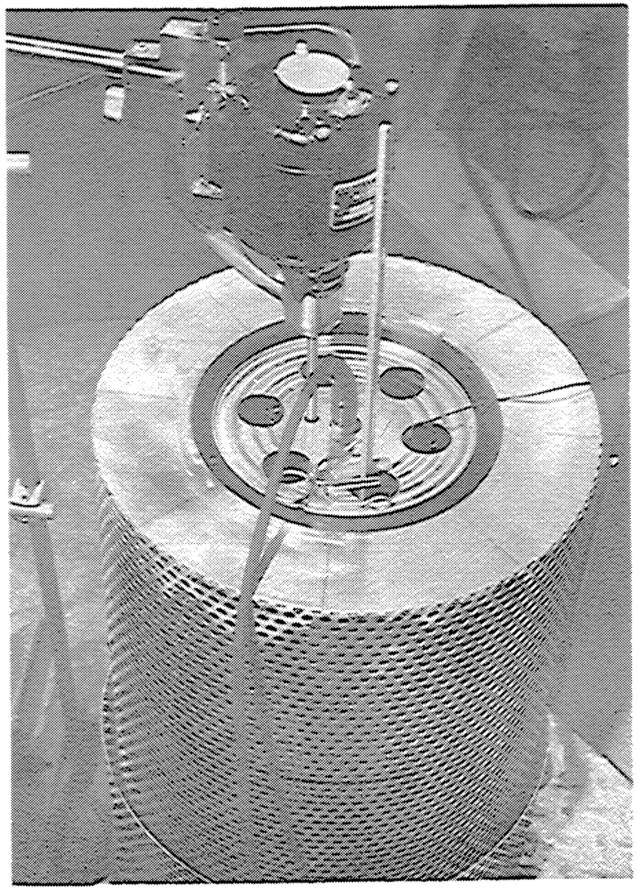


Figure III-5. Set-up for High Temperature Runs in Center Well, Showing Covered Dewar, Heater, Stirrer and Control Thermocouple Lead.

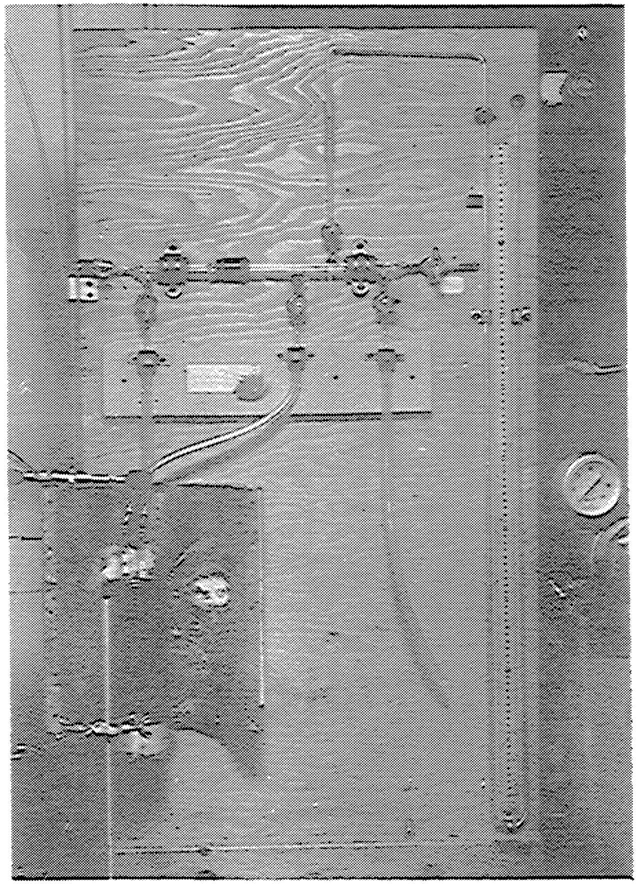


Figure III-6. Vacuum Manifold for Loading Sulfur Dioxide Into Reaction Tubes.

sulfur dioxide cylinder at the far right. A liquid nitrogen cold trap was needed to protect the vacuum pump from sulfur dioxide since the gas has a vapor pressure of about 10 mm at dry ice temperature. Dry ice was adequate, however, for condensing the SO_2 in the reaction tubes. It was used in the form of a slush bath in a mixture of 60% chloroform and 40% carbon tetrachloride, providing a temperature of $-79^{\circ}C$. This mixture was used in preference to the more common acetone-dry ice bath since it results in a more homogeneous mixture and, in addition, avoids the hazards of using an inflammable liquid in close proximity to the oxygen-gas flame used for sealing the tubes. (Due to the toxicity of the carbon tetrachloride and chloroform vapors, they should be handled with adequate ventilation, preferably in a fume hood, until cooled down by the dry ice.)

To load a reaction tube with sulfur dioxide, the serum cap was removed, the end of the tube immediately attached to the heavy wall Tygon tubing connected to one of the loading ports, the stopcock opened, and the tube evacuated. The styrene was then permitted to warm to its melting point of $-31^{\circ}C$ with the stopcock to the vacuum pump closed to prevent loss of styrene due to evaporation. The tube was then placed in the dry ice bath and refrozen with the vacuum pump stopcock only intermittently opened. Since the styrene had been preweighed, this caution was necessary to avoid losing a significant quantity. When a tube is weighed after addition of the sulfur dioxide, any loss of styrene would result in a calculated weight of sulfur dioxide which would be lower than the actual weight by an amount equal to the weight of styrene lost.

When the styrene cooled again to near the dry ice temperature, the stopcocks to both the vacuum pump and SO_2 cylinder were opened and the needle valve on the cylinder was opened slightly for several seconds to displace the air remaining in the manifold. The vacuum pump stopcock was then closed and the gas permitted to condense in the reaction tube. The needle valve was regulated to keep the manifold well below atmospheric pressure. By intermittently raising the tube so that the level mark on the glass could be seen above the surface of the bath, it was easy to tell (after some practice) just when to turn off the sulfur dioxide. The tube was then allowed to cool down thoroughly after which the stopcock to the vacuum pump was opened for a few seconds to boil off a little of the sulfur dioxide in order to further remove any non-condensable impurities.

The tube was sealed off at its neck with a small oxygen-gas flame with care taken to confine the heat to as small an area as possible. The sealed tube was placed in an empty dewar to warm slowly while the serum cap was replaced on the top part which was set aside for weighing.

When the styrene was melted, the reactants were mixed by inverting the tube about a dozen times. Care was taken to keep the reactants at or below the planned reaction temperature except after completion of the irradiation when the tube was warmed to room temperature for about two minutes to permit an accurate weighing to be made.

2. Irradiation

For the reactions at 30°C and below, the tubes were simply placed in the reaction dewar flask at the appropriate temperature, after which the flask was carried to the Co-60 source cave and put in place. The source was raised for the proper length of time, then lowered and the dewar removed. At temperatures above 30°C, the dewar had to be in place and adjusted to the reaction temperature in advance. In addition, since the dark reaction rate is appreciable at the higher temperatures, it was important to keep to a minimum the time spent in raising the tubes to the reaction temperature. This was accomplished by warming them in rapidly running hot water of the proper temperature (while wrapped in aluminum foil for protection from light) for only the length of time required to raise the contents to the desired reaction temperature. The required time had previously been determined with an unsealed tube filled with water. Immediately after the irradiation was over, the tubes were transferred to an ice filled beaker. Thus, the tubes remained at the high temperatures for only 6 or 7 minutes longer than the actual reaction time.

Since sulfur dioxide boils at -10°C and rises to a pressure of 100 psi at 48°C, and 350 psi at 95°C, a face shield, lab coat, and heavy gloves were worn whenever handling the tubes at or above room temperature. Although the sealed tubes were supposedly safe at pressures up to at least 300 psi, the Chemistry Department glassblower advised that this strength should not be depended upon.

3. Recovery of Product

After being weighed, the reaction tubes were cooled in a dry ice bath for a time long enough to reduce the temperature well below -10°C but not long enough to freeze the mixture. The tubes were then opened by scoring with a carbide glass cutting knife and pressing the molten end of a Pyrex rod against one end of the scratch. After a few light taps above the resultant crack, the tops could be lifted off without fear of glass chips falling into the tubes. This procedure is shown in Figure III-7. Some of the trouble which invalidated run Nos. 110-120 resulted from the small glass chips produced by a more forceful opening procedure.

The contents of the tubes were poured into 250 ml centrifuge tubes, each containing 150 ml of methanol and a few crystals of hydroquinone as an inhibitor to discourage any additional reaction. Since the polymer is almost completely insoluble in methanol, while the styrene monomer is miscible with it, a quantitative recovery of polymer is obtained by this method. The tubes were rinsed, first with a 50% benzene-acetone polymer solvent and then with methanol, with enough additional added to each centrifuge tube to bring the total methanol content to at least 200 ml. This dilution proved to be adequate for complete precipitation of the polymer. The necessary agitation was best achieved by means of a small battery powered cocktail mixer. In the case of those mixtures containing little sulfur dixoide, the methanol was acidified with a few drops of concentrated hydrochloric acid to prevent the formation of a colloidal suspension.

The centrifuge tubes were spun at 1500-2000 rpm on an international size 2 centrifuge for about 20 minutes. Suction was then used to remove the supernatant liquid without disturbing the polymer. Because of the high concentration of sulfur dioxide, the aspirator in a fume hood was used for this purpose. The polymer samples were washed

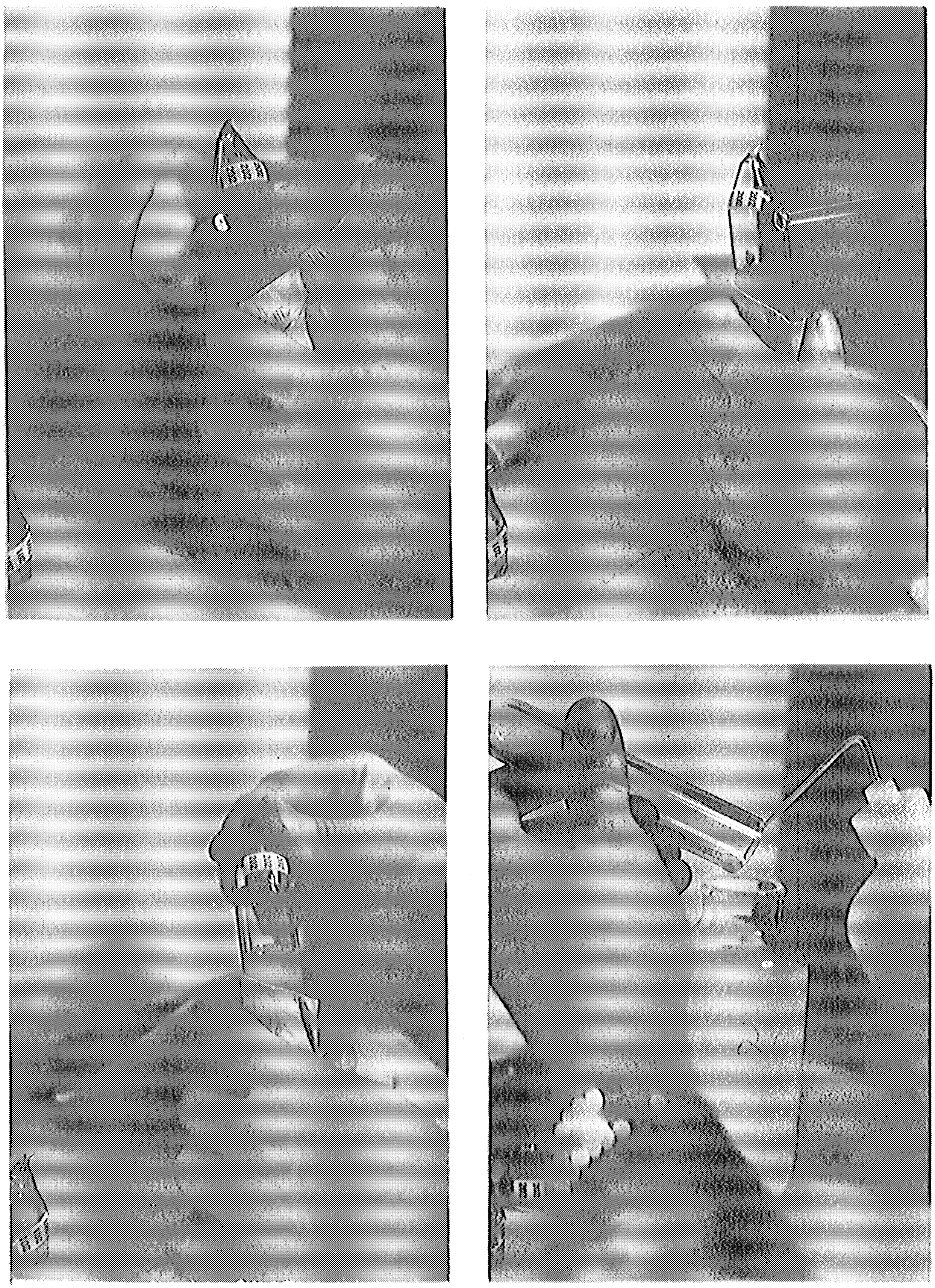


Figure III-7. Procedure for Opening Reaction Tubes.

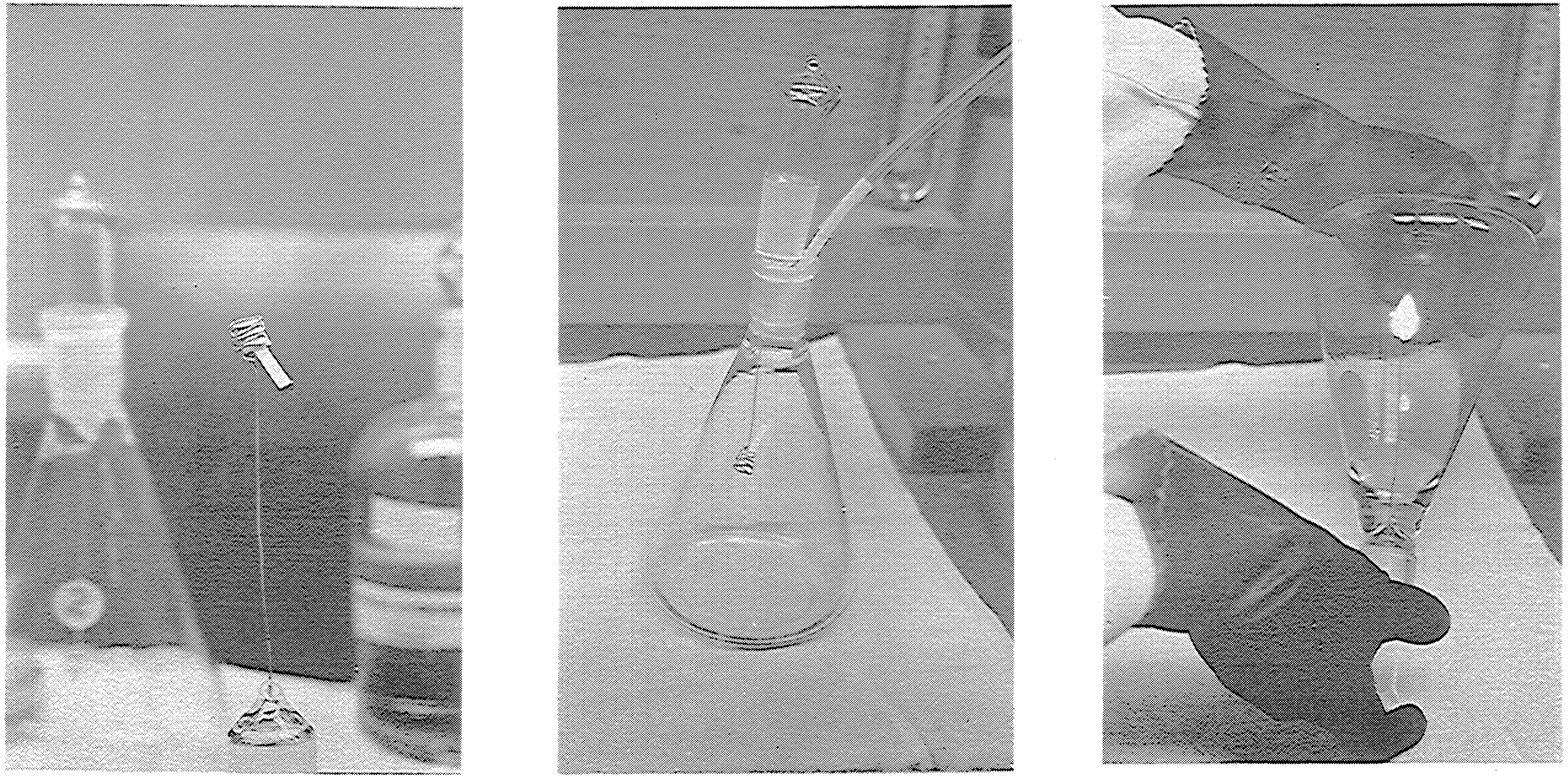
again with fresh methanol, recentrifuged and filtered (with additional washing) in preweighed Pyrex glass filtering crucibles of the Gooch type with 30 mm fine porosity fritted discs. The glass filters were dried for at least 36 hours in a vacuum desiccator connected to a vacuum pump through a dry ice cold trap. Several checks showed that no further weight was lost after this length of time. The samples were then weighed and transferred to glass vials for storage. The filters were cleaned with hot chromic-sulfuric acid and reweighed before reuse.

D. Analysis of Polymers

1. Sulfur Analysis

Polymers were analyzed for sulfur by the Schoniger combustion method.(46,88,71) Basically, the method consists of burning the sample in a closed, oxygen filled flask, absorbing the combustion gases in dilute hydrogen peroxide and titrating for the resulting sulfuric acid.

The polymer samples were first redried under vacuum and then stored in a desiccator until used. Between 0.025 and 0.030 grams were placed on a weighed piece of 3 cm Whatman No. 42 filter paper which had first been folded into a boat-like shape to retain the sample. The filter paper was then carefully folded so as to retain all of the sample and any loose particles were blown away. The paper and polymer were weighed, a 1/4 in. wide strip of filter paper inserted as a fuse, and the paper clamped to a length of platinum wire sealed to the ground glass stopper of a one-liter conical flask (see Figure III-8a).



a) Polymer Sample in Platinum Wire Clamp.

b) Purging Flask With Oxygen.

c) Burning Sample in Oxygen Filled Flask.

Figure III-8. Sulfur Analysis.

Forty ml of 3% hydrogen peroxide were added to the flask which was then purged thoroughly with oxygen (Figure III-8b).

The filter paper was ignited by means of its fuse and rapidly inserted in the flask which was then inverted to form a liquid seal at the ground glass stopper (Figure III-8c). When the combustion was completed the flask was shaken for 15 minutes to absorb all the combustion products. The stopper was then removed and washed with double distilled water. A total of 150-200 ml of water was added and then evaporated down to about 50 ml to destroy the remaining peroxide. This last step is mentioned by Lysyj(71) but not by Furman,(46) but if it is omitted a sharp end-point will not be obtained in the titration. In several cases, the solution accidently boiled down to less than 10 ml. All these runs were redone and it was found that a loss equivalent to as much as 1% sulfur occurred in these cases.

The solution was titrated in the flask with 0.01N sodium hydroxide using 4 drops of methyl red-methylene blue indicator. The sodium hydroxide was standardized with potassium biphthalate and several blanks were run using pure polystyrene in place of the polysulfone. The blanks averaged 0.10 ml.

In the first trial run, 4.25 cm filter paper was used instead of 3 cm paper. The pressure built up in the flask as a result of this larger quantity of combustable material was sufficient to lift the stopper against light hand pressure and release about one-fourth of the liquid from the inverted flask.

The combustion part of this procedure involves some risk due to the closed glass system in which the burning takes place. The risk was minimized by the use of a small sample in a large flask but the precaution of wearing a face shield, lab coat, and gloves was nevertheless followed. These precautions proved to be of value, not for this but for the following, unanticipated reason:

The flasks were filled with oxygen from the cylinder by means of a length of Tygon tubing with a short length of polyethylene tubing inserted in the end. During the last analysis the lighted fuse accidentlly brushed the end of the polyethylene tube as the tube was being removed from the mouth of the flask. The tube burst into flames and the fire rapidly travelled up the inside of the Tygon tubing against the flow of oxygen. Since there was a short length of glass tubing connecting two lengths of the Tygon tubing, a sharp pull broke the glass and cut off the supply of oxygen to the fire. In doing this, however, the experimenter's coat and face shield were hit by broken glass and molten polyethylene. It should be noted that this occurred after 90 uneventful combustions. The experimenter had begun to consider this as a perfectly safe procedure and was even tempted to neglect wearing the face shield and lab coat in the hot weather.

2. Solubility Test

Since polystyrene is soluble in benzene and according to Barb,(5,7) most styrene polysulfones are substantially insoluble, a number of product samples were tested for their solubility in benzene. About 0.05 gm of polymer was weighed into a screw capped test tube, 5 ml of benzene added, and the test tube vibrated on a pipette shaker for about 2 hours. The tube was then centrifuged and 4 ml of the supernatent solution removed and transferred by pipette to a 2 in. diameter stainless steel dish. Methanol was added to prevent the formation of a coherent film which would impede drying. The solvents were then evaporated and the precipitate dried overnight under vacuum. Since it was difficult to completely dry the insoluble fraction remaining in the test tube, only the weight of the soluble portion (actually 4/5 of this weight) was used in calculating the fractional solubility.

Two samples (Nos. 206 and 225) were analyzed for the sulfur content of both the soluble and insoluble fractions.

E. Dosimetry

Gamma radiation dose rates for all reaction conditions were determined by the ASTM "Tentative Method of Test for Absorbed Gamma Radiation Dose in the Fricke Dosimeter" (ASTM Designation: D1671-59T).(2) It is recommended over the following range of conditions:

Total Dose - 2 to 40 kilorads
Dose Rate - Up to 10^7 rads/hour
Temperature - 0 to 50°C
Energy - 0.1 to 2 Mev.

The method is based on the oxidation of ferrous ammonium sulfate and the spectrophotometric determination of the ferric ion concentration. It is a slight refinement of the technique of Weiss,(117) the only significant difference being the substitution of oxygenation for aeration.

The dosimetric solution contains 0.001 M ferrous ammonium sulfate and 0.001 M sodium chloride in 0.4 M sulfuric acid which has been saturated with oxygen. It is important to keep the solution free from organic material although the addition of the sodium chloride reduces the effect of this contamination. After irradiation, the solution is analyzed for ferric ion in a Beckman Model DU spectrophotometer with hydrogen lamp attachment and 1 cm matched quartz cells (or equivalent equipment). The optical densities are determined at 305 mμ with a slit width of 0.5 mm. The extinction coefficient varies slightly among individual instruments so that for accurate work the individual spectrophotometer should be calibrated against standard ferric sulfate solutions. The extinction coefficient for ferric ion also has a temperature coefficient of +0.7% per ^{o}C making temperature control, or at least temperature measurement, desirable.

In the present work, the dosimetry was performed in the actual glass tubes used for the experiments. A group of used tubes were cleaned with chromic-sulfuric acid solution and reserved for this purpose after their broken edges had been fire polished. The tubes were filled to levels corresponding to the various concentrations of sulfur dioxide used. They were irradiated in the same positions and under the same conditions as the actual experimental runs with the exception that all of the dosimetric runs were made at room temperature.

For convenience, a stock solution of 0.1 M ferrous ammonium sulfate, 0.1 M sodium chloride, and 0.4 M sulfuric acid was prepared. It was diluted 1:100 before use and stored in a dark bottle in a refrigerator. On the same day as a dosimetric run, a liter of 0.4 M sulfuric acid was prepared with double distilled water and oxygenated by bubbling tank oxygen through it. Ten milliliters of stock solution was then added. Any solution remining at the end of the day was discarded.

Before taking samples for the spectrophotometric measurements, the tubes (which were closed with rubber stoppers covered with Saran Wrap) were inverted several times to mix the solution. The slightly erratic results obtained before this step was instituted were presumably due to the fact that the bottoms of the tubes were in a slightly higher radiation field than were the tops. Mixing insured that a true average dose was measured in each case.

The spectrophotometer was calibrated against standard ferric sulfate by others in this laboratory.(48) All the work was done with the instrument located in an air conditioned room (an animal room) for temperature control. In addition, accurate temperature measurements were made of the solutions at the time of use. A G value of 15.6 molecules oxidized per 100 electron volts absorbed was used in the calculations since it is considered the best value for Co-60 radiation.(1) The ASTM standard recommends the use of $G = 15.5$.

The extinction coefficient determined by the calibration was found to be 2140 at 22°C. It is defined as the optical density/mole per liter/cm. of path length. From this value and the temperature coefficient, the following dose factors were calculated. The temperature is that of the solution when measured in the spectrophotometer. These factors were used for all of the dosimetry measurements.

T	Dose Factor
°C	Kilorad/Optical Density
21	28.5
22	28.3
23	28.1
24	27.9
25	27.7
26	27.5
27	27.3
28	27.1

IV EXPERIMENTAL RESULTS

A. Range of Variables

Almost all of the reactions were run in the center well of the Cobalt-60 source at the Phoenix Radiation Facility (P.R.F.) which gave a dose rate of 1200 to 1460 rad/min. The reaction was the most thoroughly investigated at 0°C with the initial SO_2/styrene molar ratio ([S]/[M]) varying from 0.03 to 1.1 and reaction times from 15 minutes to 28 hours. Less extensive work was done at temperatures ranging from -21° to +95°C.

A few runs were made at other radiation intensities but only at 0°C and [S] /[M] = 0.5. A dose rate of 6040 rad/min was obtained in the source at the Phoenix Memorial Laboratory (P.M.L.). Outside the center well of the P.R.F. source 128 rad/min was obtained at 30 cm from the source and 33.4 rad/min at 70 cm.

The reactant mixtures for all runs consisted only of styrene and sulfur dioxide; no solvents were used.

Several dark runs were made at 0°C and one at 60°C to determing the extent of thermal initiation. In addition, some pure styrene was irradiated at -21, 0, 48, 64, and 68°C.

Table I gives the results of all the usable experimental runs. The following runs were omitted for the reasons given:

Number 110-120	These were done to test out the proposed procedure. The styrene was distilled before the final modification of the still and the tube opening method resulted in glass chips being mixed with the polymers.
Number 123	Air leak in reaction tube.
Number 179, 180	Large temperature variations during irradiation.
Number 199	Polymer not recovered.
Number 214, 221	Contamination of reactants during loading.

B. Polymerization Yields

1. Description of Products

Observation of the reaction mixtures after irradiation, but before removal from their reaction tubes, showed that the polymers were completely soluble only at high SO_2 concentrations. Low doses resulted in slight cloudiness which increased at higher doses. Some precipitation occurred in the 200 minute runs except at the very high [S]/[M] ratios. Larger amounts of precipation occurred in the 495 minute runs and a very large amount in the 1660 minute run. In all cases the precipitate had the appearance of a viscous fluid of sufficiently greater density that it could be seen as a phase distinct from the unprecipitated suspension.

Except when the yield of polymer was low, the appearance of the polymer after precipitation in methanol depended largely on the technique used in pouring the reaction mixture into the methanol. When it was done properly -- poured slowly while the methanol was still in motion from prior stirring, a white flocculent precipitate resulted.

When this step was not done carefully, a tough lumpy mass sometimes resulted.

After drying, the polymers were, in all cases, recovered as white powders, though in a few cases, one or two small pieces of yellow tinted polymer could be seen. The consistency, before removal from the filtering crucibles was usually either a fluffy mass or a soft dense cake. The lumpy masses, resulting from improper precipitation, usually dried as porous lumps which could easily be broken up, but occasionally, hard dense pieces were obtained.

Samples of four polymers were tested for heat stability by heating them in an oven at 140, 150, 180, and 200°C. The results were as follows:

Run No.	n	140°C 9 hours	150°C 2 1/2 hours	180°C 6 hours	200°C 2 1/2 hours
184	2.2	no change	no change	yellowed	melted into dark yellow lumps, 1% weight loss
185	1.8	no change	no change	yellowed and shrunk	melted into black glassy film, 9% weight loss
188	2.9	no change	no change	very slightly yellowed	melted into light yellow lumps, 0.6% weight loss
222	1.6	no change	no change	no change	melted into black glassy film, 11% weight loss

These samples were chosen to represent both extremes of polymer composition; n = moles of styrene/mole of SO_2 in the polymer. The same samples were used for all four temperatures; they were cooled and weighed after each heating.

2. Results at 0°C

The weight fractional yields (P/S+M) at 0°C are shown in Figure IV-1 as a function of [S]/[M]. All runs at this temperature that were made in the PRF center well (see part A) are included. Since the dose rates for these runs vary from 1250 to 1460 rad/min., all the points on the graph are normalized to a nominal intensity of 1400 rad/min. by multiplying each value of P/S+M by $(1400)^{1/2}/I^{1/2}$ where I is the dose rate for the particular run. This assumption of square root dependence is explained in the next chapter but since it is used here over such a narrow range no appreciable error would be introduced even if the data were to deviate considerably from the assumption. The individual distillation batches are shown to permit any effect of differences in styrene purity to be seen. The only noticeable effect appears in the 15 minute curve where batch 3 appeared to have given lower yields.

The effect of the reaction time is more clearly shown in Figure IV-2 which is a cross plot of Figure IV-1 giving P/S+M vs. reaction time for [S]/[M] = 0.5. It shows that a linear relationship holds from 30 minutes (42 kilorads) to at least 500 minutes (700 kilorads).

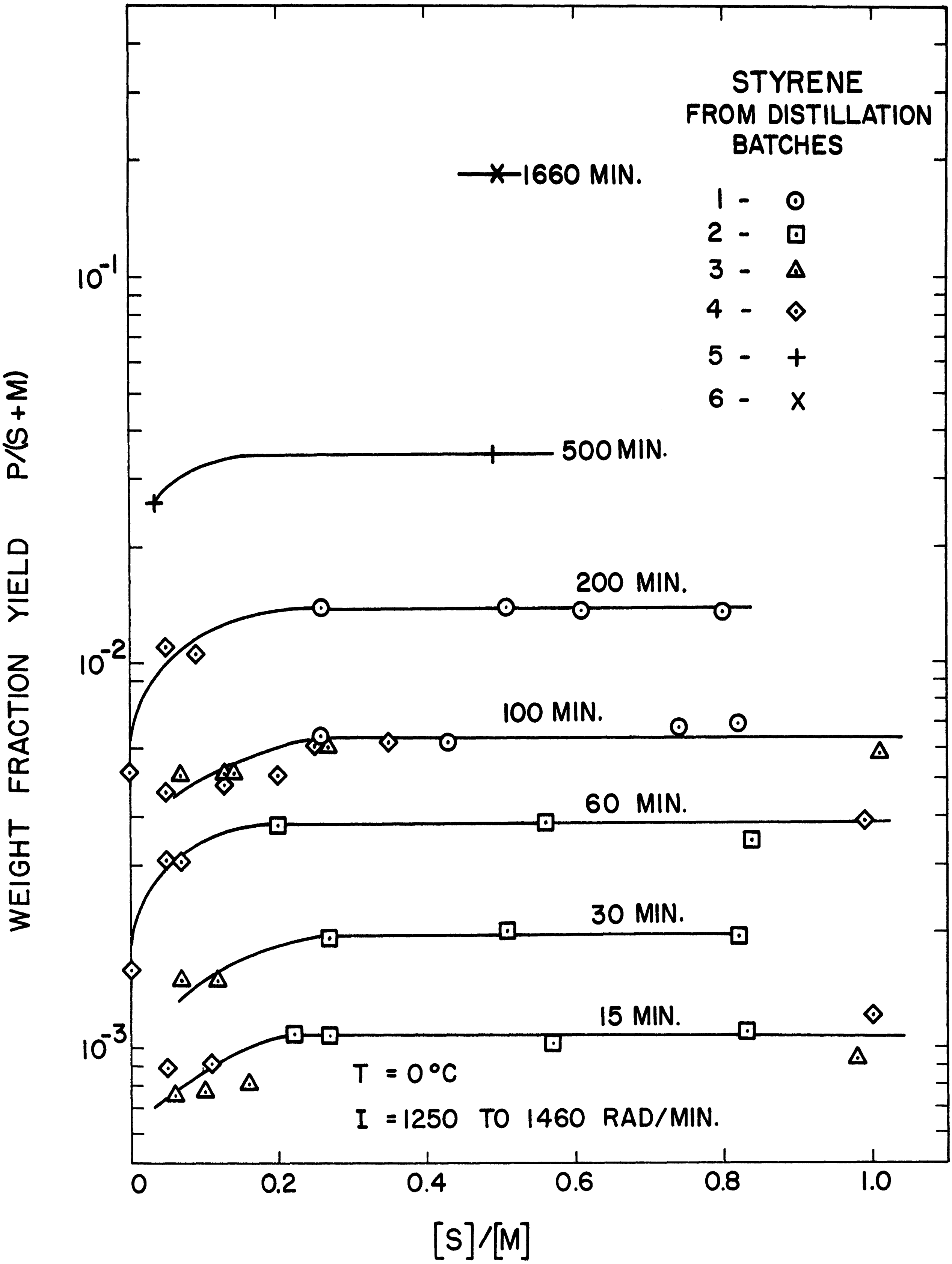


Figure IV-1. Weight Fraction Polymerized vs. Reactant Ratio for Each Irradiation Time. Yields are Normalized to a Dose Rate of 1400 rad/min.

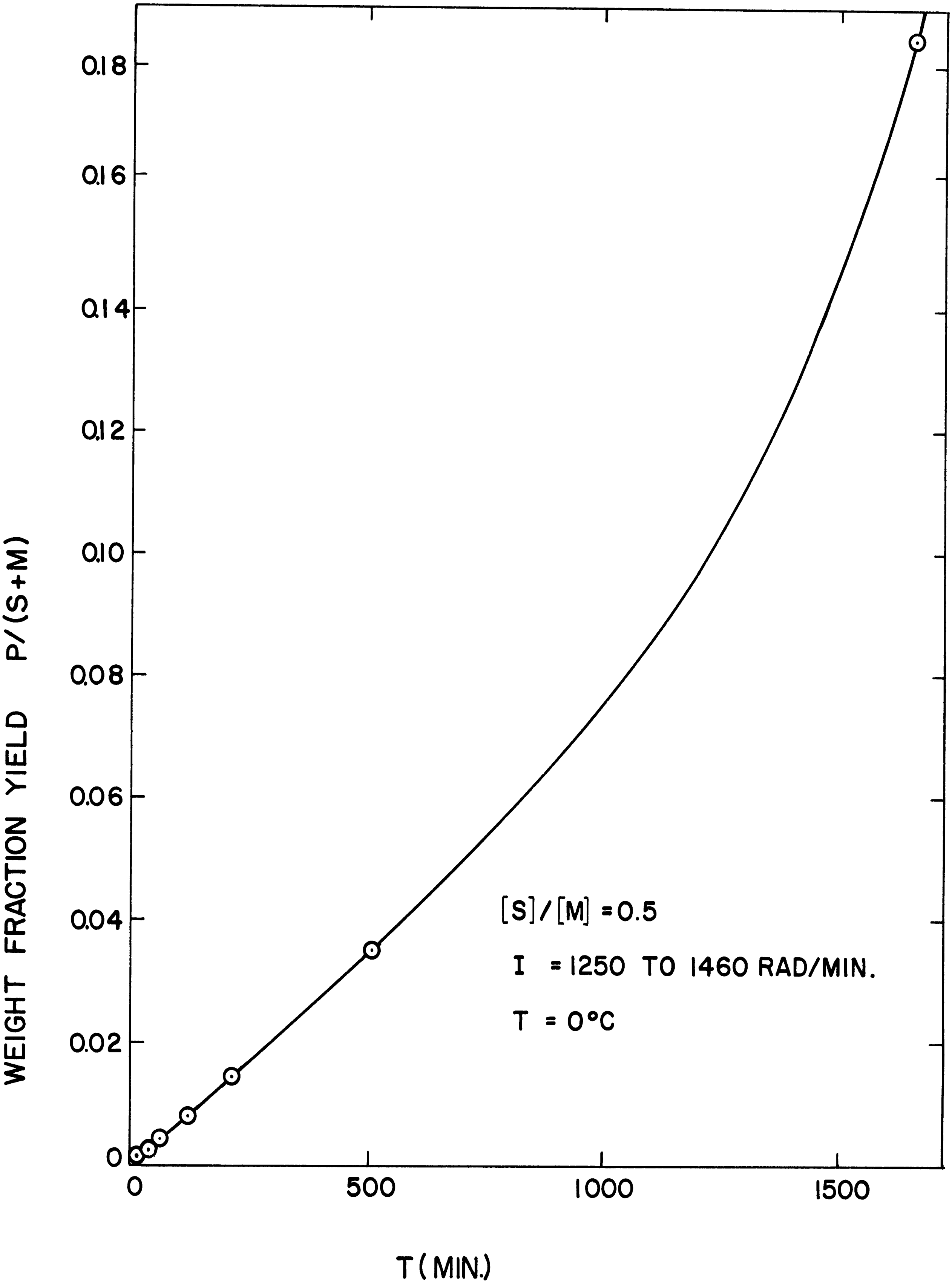


Figure IV-2. Weight Fraction Polymerized vs. Irradiation Time for [S]/[M] = 0.5, Interpolated from Figure IV-1.

Figure IV-3 shows the variation of reaction rate (P/S+M/min.) with gamma dose rate at 0°C. The rate for 1400 rad/min. is an average rate taken from Figure IV-2. The data in this form correspond closely to the expected $I^{1/2}$ dependence for free radical polymerization.

3. Temperature Variation

Reactions were run at temperatures of -21°C to +95°C. In Table I it will be noted that, starting with run number 204, the higher temperatures are given to the nearest 0.1°C. These temperatures were read from a mercury thermometer marked in tenths of a degree which was inserted into an open, water-filled tube in the dewar (see Figure III-5). All previous temperatures above 30°C were read from the temperature control thermocouple as recorded on the chart. These temperatures may be in error by as much as ± 1°C.

Figures IV-4 and IV-5 show the effects of temperature on the reaction rate. The rate, expressed as weight fraction polymerized (P/S+M)/megarad is shown in Figure IV-4 and the value $(S_p/S+M)$/megarad (S_p = grams SO_2 in polymer) is shown in Figure IV-5. The 0° points are not plotted. The two 10 minute runs (13200 rad) at 50° and 85° show a much larger apparent rate than do the longer runs.

In Figure IV-6 the rates from Figures IV-4 and IV-5 are plotted against temperature for [S]/[M] = 0 and 0.5, the limited data for reactant ratios other than 0.5 precludes a more detailed presentation. It should be noted that the 0°C point appears high on the

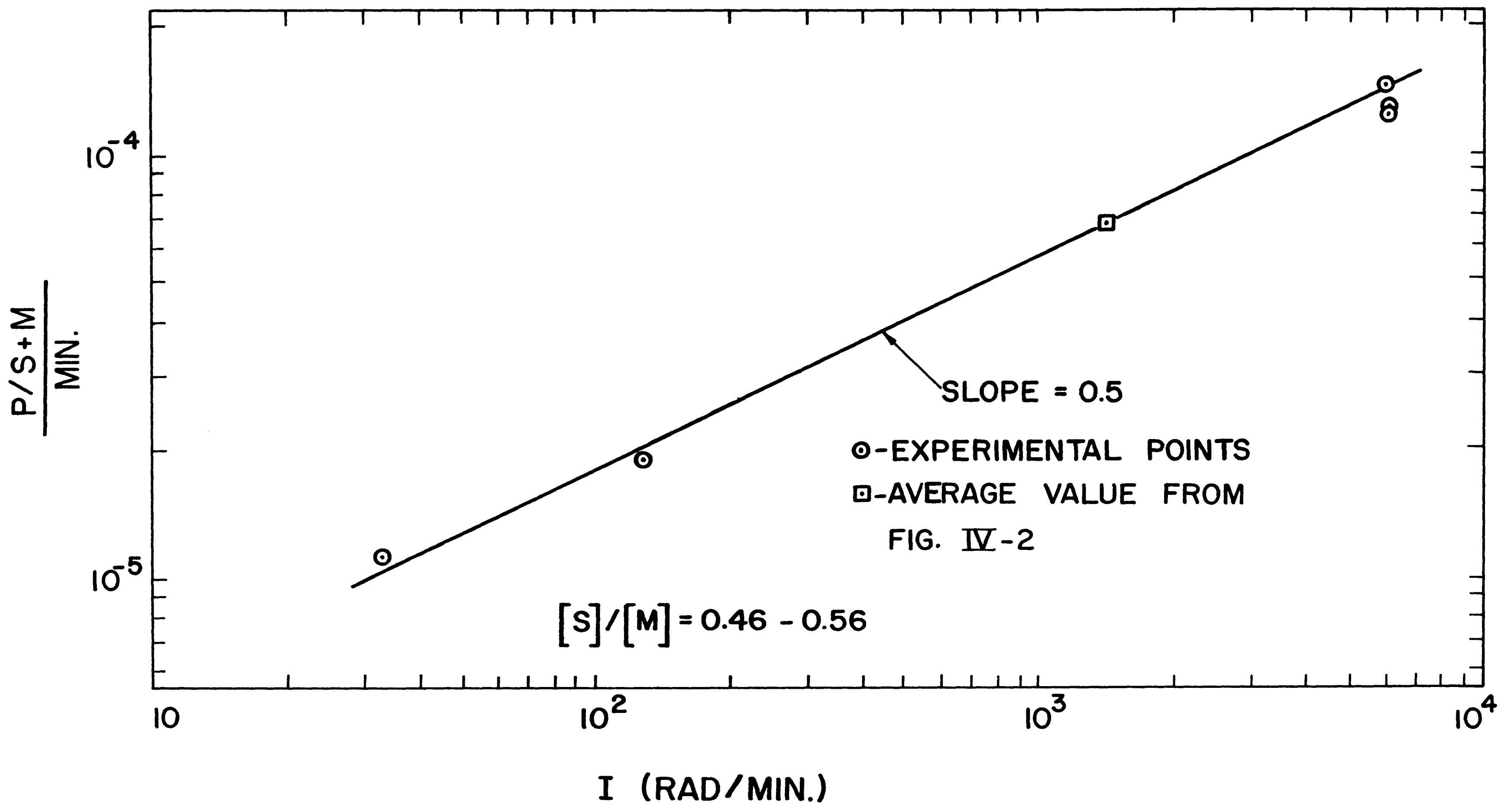


Figure IV-3. Rate of Polymer Formation vs. Radiation Intensity. Point at $I = 1400$ is the Slope of the Straight Line Portion of Figure IV-2.

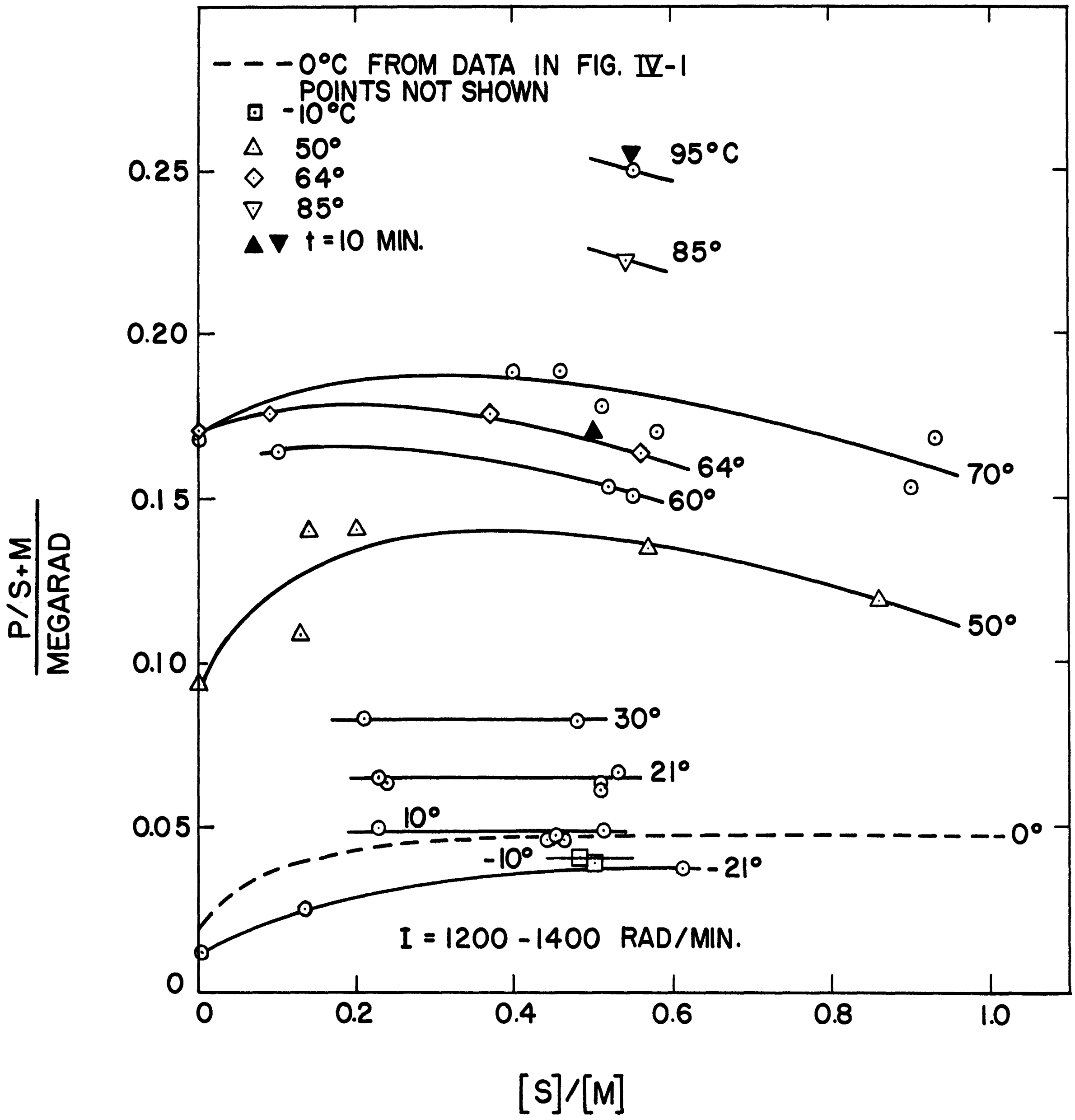


Figure IV-4. Polymer Yield per Megarad vs. Reactant Ratio for all Temperatures. Individual Points for 0°C are not Shown.

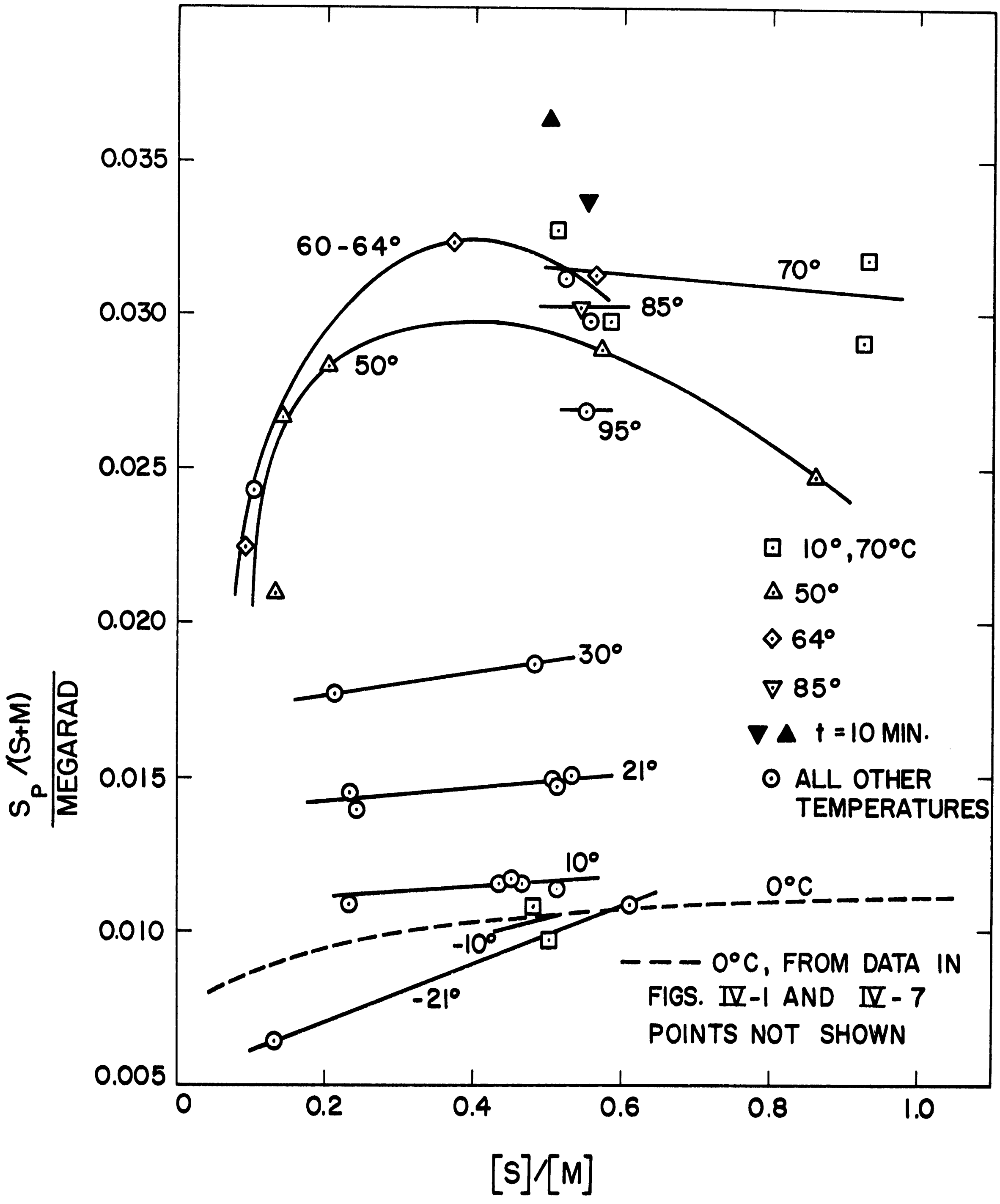


Figure IV-5. Yield of Sulfur Dioxide in Polymer per Megarad for all Temperatures. S_p = Grams of SO_2 in Polymer.

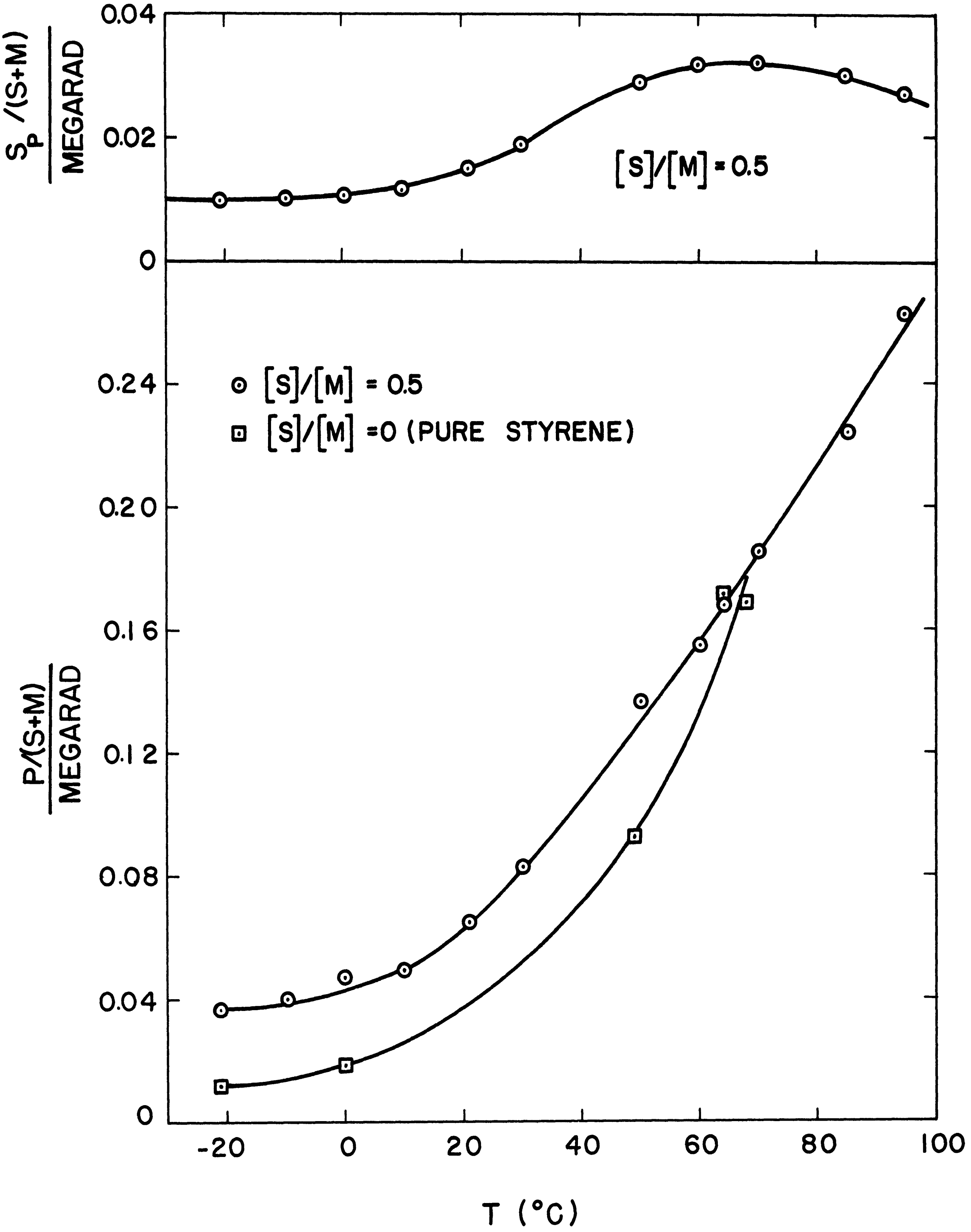


Figure IV-6. Yields per Megarad vs. Temperature for [S]/[M] = 0.5 (Interpolated from Figures IV-4 and 5) and for Pure Styrene.

P/S+M plot but not on the S_p/S+M plot. This was the first evidence of a difficulty which also shows up in the composition and solubility data and which will be discussed in detail in Chapter V.

4. Errors

Two kinds of errors resulting from mistakes in experimental procedure are noted in Table I. In three runs, some polymer was lost during recovery but the amounts were too small to be detected in the results. In no case could it have exceeded 5%. A more serious mistake was the omission, in eight runs, of one of the weighings needed to calculate the reactant weights. In run number 211, the weight of styrene is missing while in other seven runs the weight of sulfur dioxide is missing. However, since the weight of styrene can be estimated to within ± 2% and the weight of SO_2 within ± 10% (except at low SO_2 concentrations), it was still possible to use the results of these runs.

In the description of the loading procedure in Chapter III, the possibility of loss of some styrene while degassing under vacuum was discussed. In those runs with very low concentration of sulfur dioxide, this could lead to substantial underestimates of SO_2 concentrations. In the runs involving only styrene, it was possible to check for weight loss by comparing the weights before and after degassing and sealing the tubes. The losses were:

No. 160	0.11%	No. 203	2.4%	No. 208	0.00%
No. 161	0.5%	No. 204	0.34%	No. 209	0.00%

The underestimate of the SO_2 concentration at $[S]/[M] = 0.05$ due to a 1% loss in styrene would be 25% so that the situation is potentially significant. The above runs, however, probably represent a maximum loss since no particular effort was made to reduce evaporation in these cases. The much greater care taken with the low SO_2 concentration runs should have kept the styrene losses very low since the zero losses from numbers 208 and 209 show that this is possible.

If, after the polymer is dried, there remains some styrene monomer trapped in the solid, an overestimate of the yield and an underestimate of the sulfur content of the polymer would result. This would be most likely to occur in the occasional dense lumps noted in Section IV-B-1. Since these lumps were not used in the sulfur analysis, only the effect on polymer weight would be detected. Although the existence of this error cannot be ruled out, no evidence of it was detected.

A more important source of error is the hydroscopic nature of the dried polymers. The polymer samples, particularly those of fluffy consistency, absorb water rapidly from the air. Since this effect was not fully appreciated at the start of the experimental program, it is likely that some of the polymer yield weights are slightly high as a result of premature removal from the desiccator.

C. Analyses

1. Sulfur Determination

Most of the polymer samples were analyzed for sulfur. Figures IV-7 and IV-8 show the results as percent sulfur in the polymer as a function of the reactant ratio [S]/[M]; Figure IV-7 presents the 0°C data and Figure IV-8 the data at other temperatures.

The 0°C data is presented using a different symbol for each reaction time at 1400 rad/min and separate symbols for each of the other three dose rates. In addition, those polymers which were less than 10% soluble in benzene are signified by a filled symbol. This detailed differentiation is given to aid in interpreting this data, which at first appeared to show little, if any, relationship at all.

While deferring a full discussion until the next chapter, several relationships can be seen here:

1. The low solubility polymers have a substantially higher sulfur content than those with higher solubilities.

2. The polymers from the shorter runs contain less sulfur than those from runs of at least 100 minutes.

3. The polymers from the 495 and 1660 minute runs and those prepared at low dose rates have high sulfur content and low benzene solubility.

4. The low solubility polymers show an increase in sulfur content with an increase in SO_2 concentration in the reactant mixture.

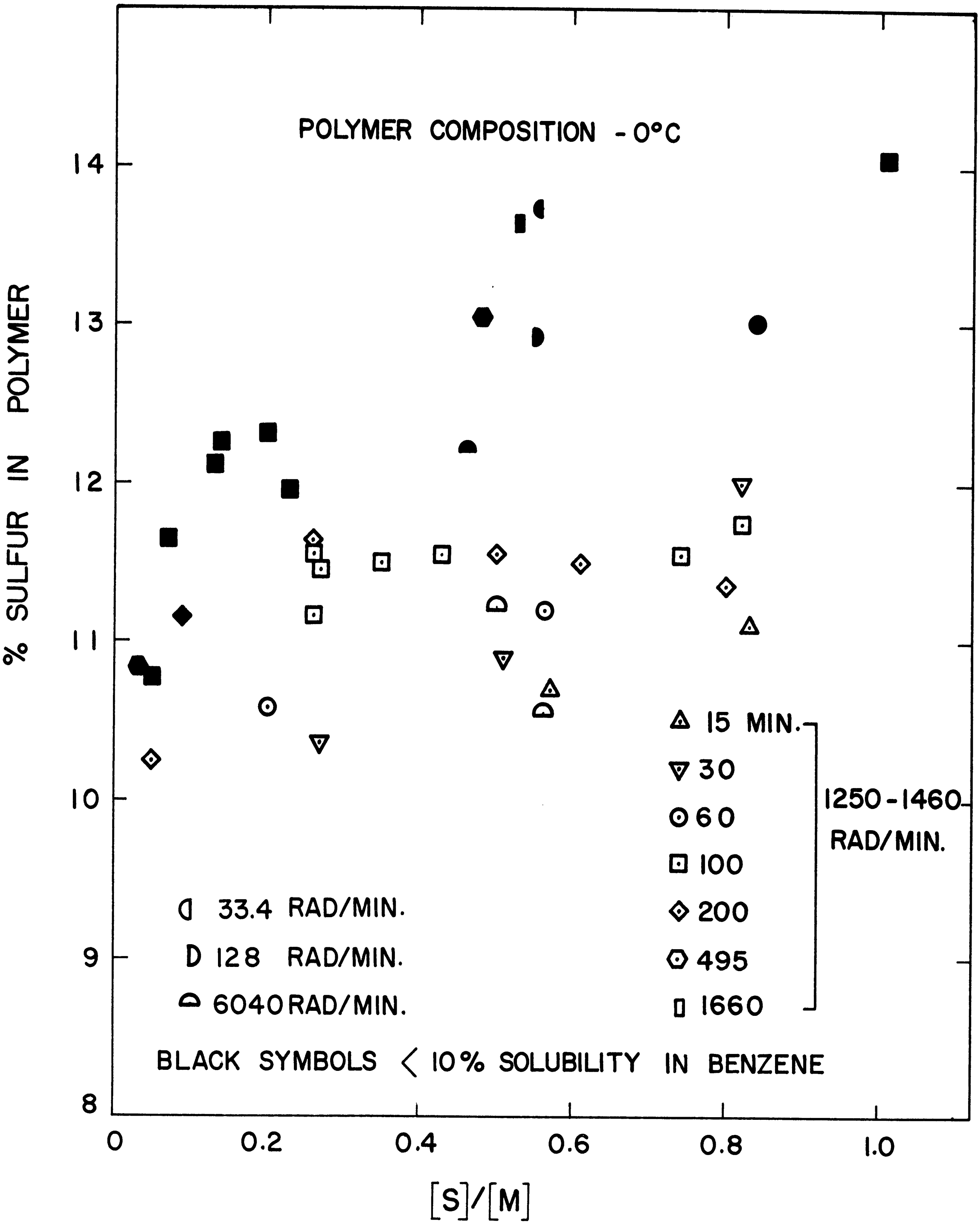


Figure IV-7. Polymer Composition vs. Reactant Ratio at 0°C.

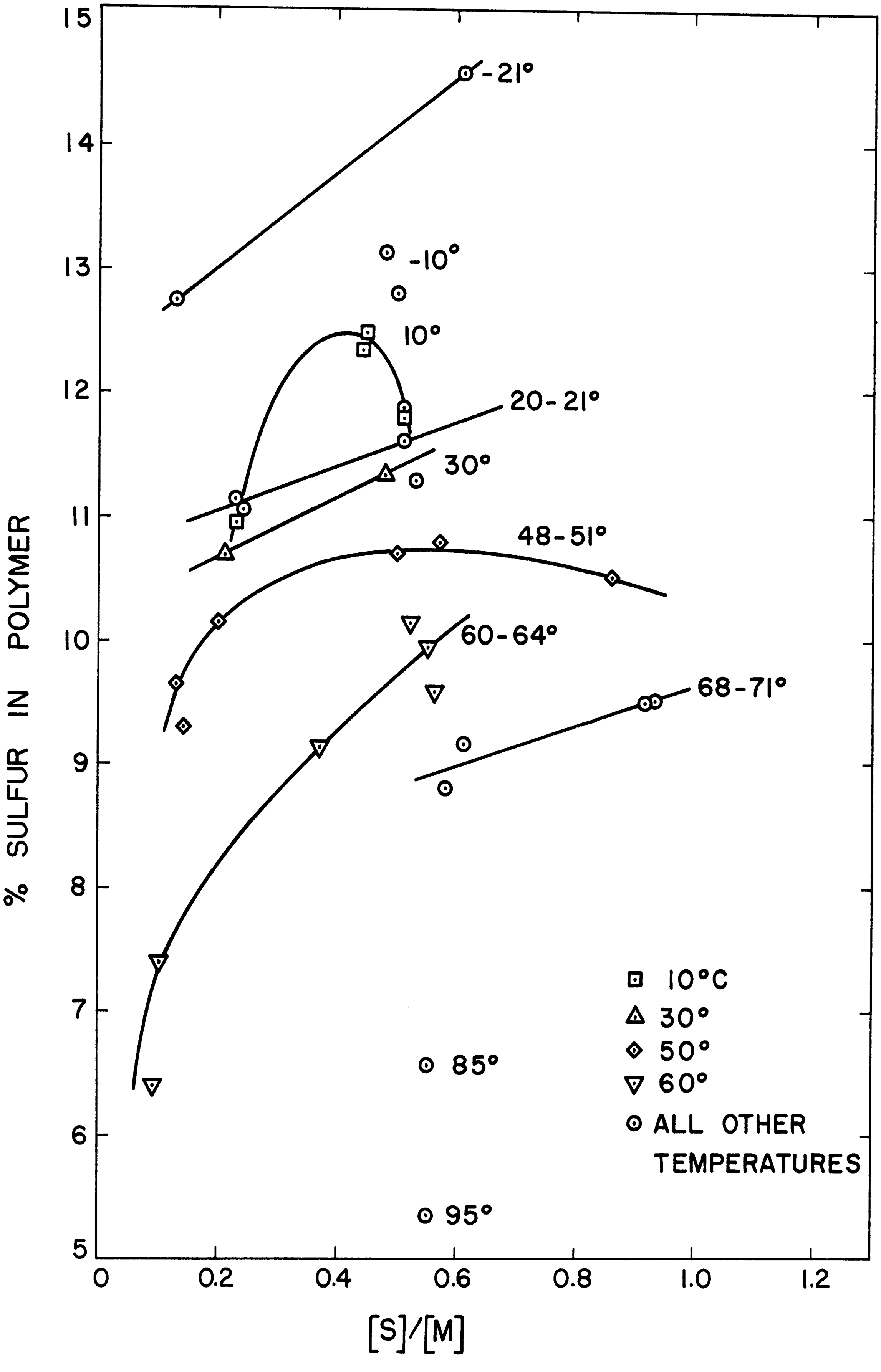


Figure IV-8. Polymer Composition vs. Reactant Ratio at all Temperatures Except 0°C.

Figure IV-8 shows the sulfur content of polymers prepared at temperatures from -21°C to 95°C. The 0°C data is omitted to improve the readability of the graph. The lines are drawn simply to identify the isothermal points; their shape and slope are not meant to have any particular significance. Note the steady decrease in % sulfur with increasing temperature and the sharper drop above 70°.

The sulfur analyses were subject to one obvious non-random error. In two cases, a small ball of fused, unburned polymer was observed in the flask after the ignition. In one of these cases (No. 131) there was sufficient polymer to repeat the analysis; the results of the first and second determinations were 11.18% and 11.34%. In the other case (No. 140) there was not enough product to repeat the analysis, but the result, 9.59% sulfur, was lower than would be expected from Figure IV-7.

This method of analysis depends for its accuracy on the sample remaining in the platinum wire clamp until it is completely burned. In the above two cases and perhaps in others a small piece of molten polymer dropped from the wire before the combustion was completed. Since these small pieces are not easily seen it is likely that a few of the results are low due to this error.

Four blanks were run using polymer from number 203 and 208 which were pure styrene runs. These four runs required 0.10, 0.10, 0.12 and 0.10 ml NaOH for the titration. Standardization with potassium biphthalate gave a NaOH concentration of .00991 N.

As a check on the accuracy of the method, two other samples were analyzed. One was a sample of hexene-1 polysulfone prepared by Bray(12) in 1957 and analyzed by the Parr bomb method. Bray reported an analysis of 21.0% sulfur. The other sample was sulfonal, $(CH_3)_2C(SO_2 \cdot C_2H_5)_2$ with a theoretical 28.1% sulfur content. Values of 19.5% and 27.4% respectively were obtained for these samples but since the sulfonal sample was of unknown purity and both samples were several years old, it would not be justified to conclude from these results that this technique results in low values.

Polymer compositions were also compared with results reported by Barb(5,7) for styrene polysulfone prepared at 20° and 60°C. The compositions check closely and do not show any tendency toward low values. (See Chapter V for the details of this comparison.) Lysyj(71) reported results for analyses of several known sulfur compounds by this method with a mean of 100.15% recovery and a standard deviation of 0.57% for samples of 5-10 mg.

2. Solubility Test

Most of the polymer samples which were analyzed for sulfur were also tested for solubility in benzene. This was done in view of Barb's(5) finding that the copolymer, with n = 2, was insoluble in benzene and that for n greater than about 3.7 (7.5% sulfur) the copolymers were soluble in it. The results are shown in Figure IV-9

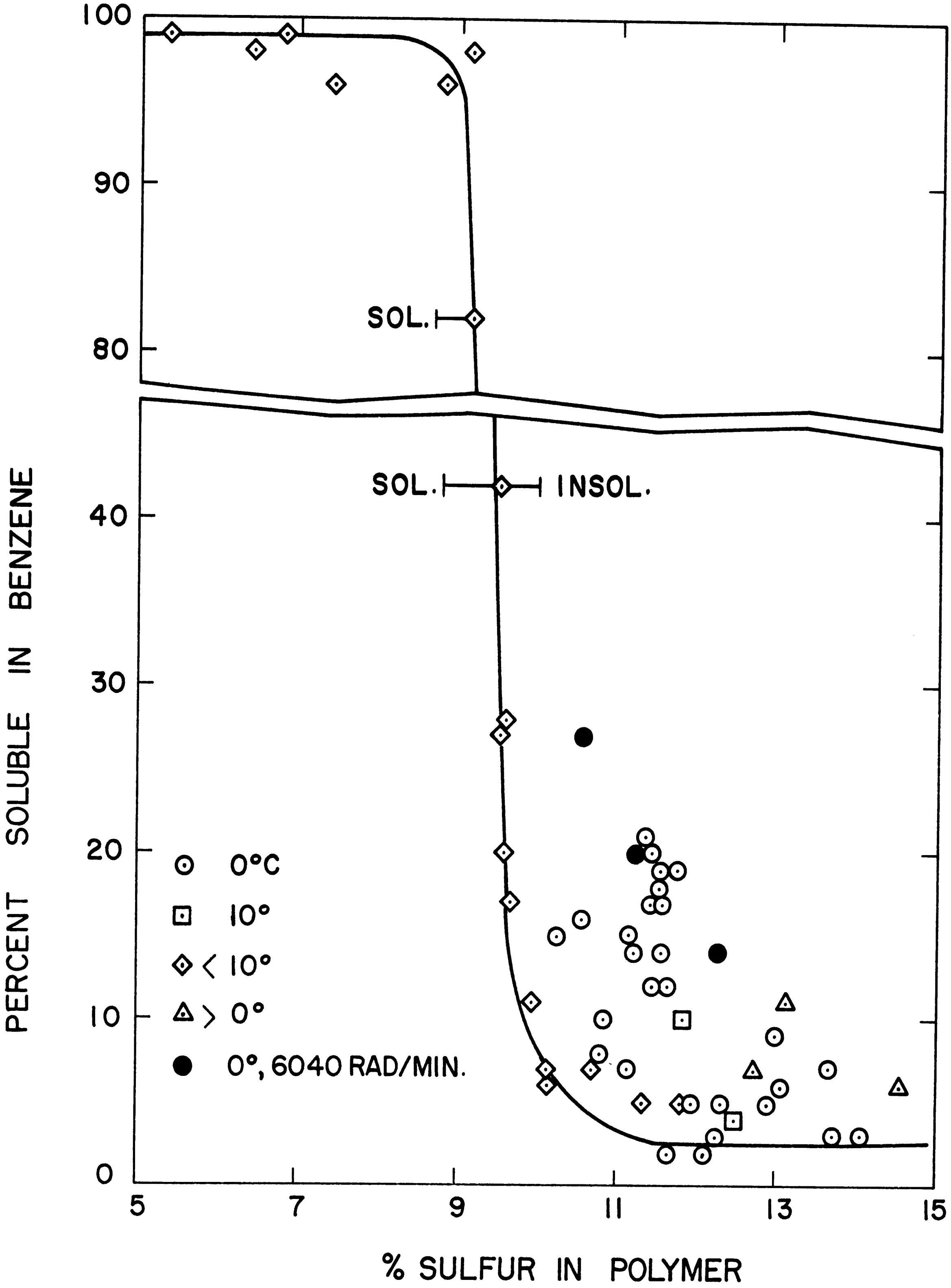


Figure IV-9. Solubility of Polymer in Benzene vs. Polymer Composition. Curve is Drawn Through Minimum Solubility Points. Compositions of the Soluble and Insoluble Fractions of No. 225 and the Soluble Fraction of No. 206 are Indicated.

which plots the % soluble vs. % sulfur in the polymer. The curve is drawn through the points of minimum solubility. The soluble and insoluble fractions of one sample and the soluble fraction of another were analyzed separately for sulfur; the results are shown on the graph. The significance of the partial solubility of some of the polymers of high sulfur content will be discussed in the next chapter. Note the high solubility of the 6040 rad/min points.

The solubility results were subject to two important non-random errors. Most of the polymer samples possessed a physical structure that was easily dispersed in the benzene by the violent agitation. A few, however, contained small, hard pieces that remained intact, resulting in incomplete solution of the soluble fraction of the polymer. To determine the possible magnitude of this effect a second test of No. 129 (19% soluble) was performed using crushed (but not ground) pieces from a hard lump of polymer; a value of 11% was obtained. Few, if any, samples should show this large an error. The second source of error resulted from the failure to maintain the same temperature for all the tests. The temperature range was approximately 20°C to 30°C.

Table I shows the results of duplicate solubility determinations of several of the polymer samples. Except for Nos. 206 and 225, the two samples closest to 50% solubility, the duplicates were within 2%.

3. Density Determination of Reactant Mixtures

In order to avoid the assumption of additive volumes, the densities of styrene-sulfur dioxide solutions were measured at various temperatures. This was done by the following method:

Weighted amounts of styrene and SO_2 (with a little hydroquinone to prevent polymerization) were sealed into glass tubes. The tubes were then held at constant temperature and the level of the solution carefully marked for each temperature. After the tubes were opened and cleaned the volume at each mark was determined gravimetrically with water.

The results are given in Figure IV-10. The measured densities are greater than those calculated on an additive volume basis and the discrepancy increases with temperature. The measured densities were estimated to be accurate to ± 0.01 g/cc. The top graph shows the raw data plotted as density vs. temperature for the compositions of the four tubes. The lower graph is a cross plot of the top curves, showing the density vs. reactant composition for various temperatures.

D. Dosimetry

The results of the ferrous sulfate dosimetry are given in Table II. Determination of the dose rates in the center well of the PRF source presented some complications caused by the nonuniformity of the radiation field and the lack of symmetry of the field with

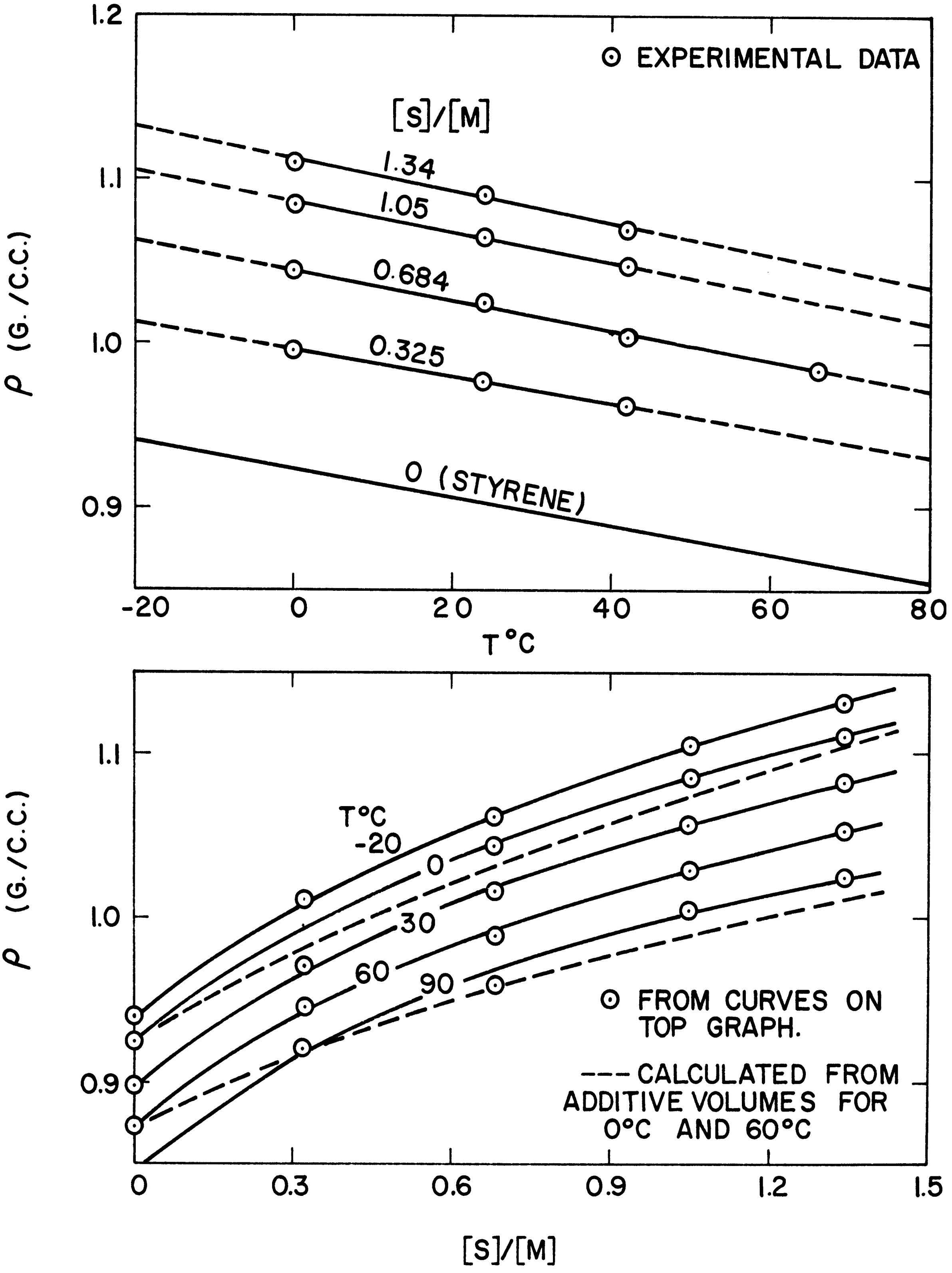


Figure IV-10. Density of Reactant Solutions. Top - Experimental Results. Bottom - Cross Plot of Top Curves; Density vs. Reactant Ratio as a Function of Temperature.

respect to the samples in the reaction tubes. The use of the large dewar flasks A and B (see Chapter III) resulted in the reaction samples being placed with the bottom of the samples about 11 cm. above the base of the center well which is almost exactly the plane of maximum dose rate. Since the same quantity of styrene was used in all cases, the height of the samples in the tubes varied with the quantity of sulfur dioxide added and the average (and minimum) dose rate decreased as the ratio [S]/[M] increased. A map of the radiation field in the center well, prepared by J. T. Graikoski and N. C. Kothary(48), is reproduced in Chapter II with a typical reaction tube superimposed.

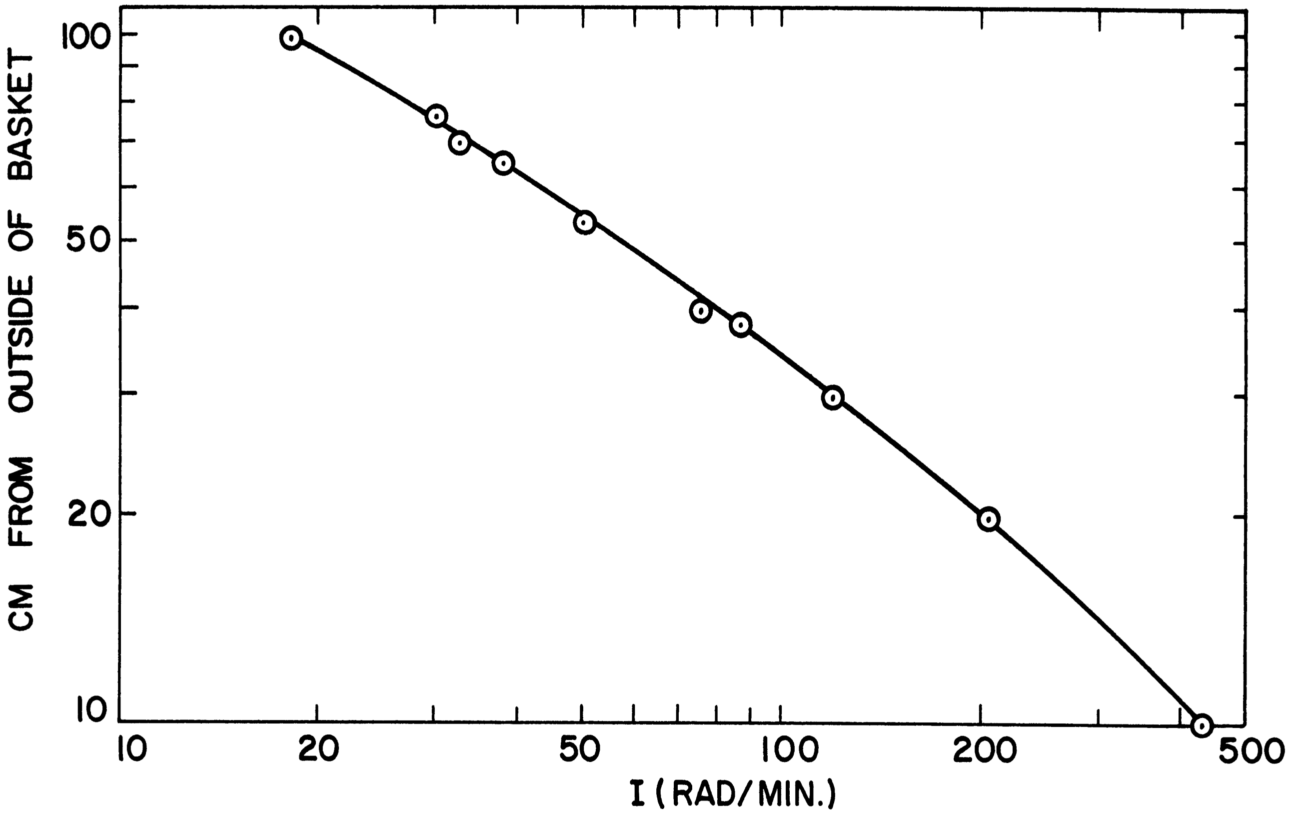
It was necessary, therefore, to determine the dose rate for various heights of solution in the reaction tubes. It had been determined approximately that [S]/[M] = 0 corresponds to 3.3 inches of solution, [S]/[M] = 0.5 to 4.0 inches and [S]/[M] = 1.0 to 4.7 inches. The dosimetry, therefore, was done with various depths of solution in the tubes. In the first runs, the solutions were poured into the spectrophotometer cells without first being mixed. Since the radiation level was highest at the bottom and lowest at the top, this practice resulted in excessive scatter in the data. Accordingly, in the final runs the dosimetry solutions were agitated after irradiation by inverting the tubes several times. This procedure did succeeed in improving considerably the reproducibility of the data, indicating that the previous procedure had not obtained a true average dose for each sample.

Only this last data was used. The results are shown in Figure IV-11 together with the results of the dosimetry outside of the center well, on the north side of the source basket.

The top curve shows the dose rate outside of the center well at the horizontal mid-plane of the source. The distance was measured from the outside of the source basket at the mid-plane (see Figure II-2). The lower curve shows the dose rate in the center well for various heights of solution in the reaction tubes. The effect of the minor differences in geometry of dewars A and B can be seen.

The dosimetry in the center well of the source at the Phoenix Memorial Laboratory (PML source) was complicated only by the short irradiation times necessitated by the high dose rates. Timing is more difficult with this source due to the slow electric motor drive. To correct for this, a previously reported value of 10.5 seconds equivalent "up" time for the up and down correction was used. The measured "up" time therefore was 3 min. 49.5 sec. instead of the 4 minutes used in the computations. Unlike the positioning difficulty in PRF center well, the samples here were able to be positioned symmetrically in the radiation field.

Except for the unmixed samples described above and the very low optical density samples among the determinations outside of the source basket, reproducibility was within ± 1%.



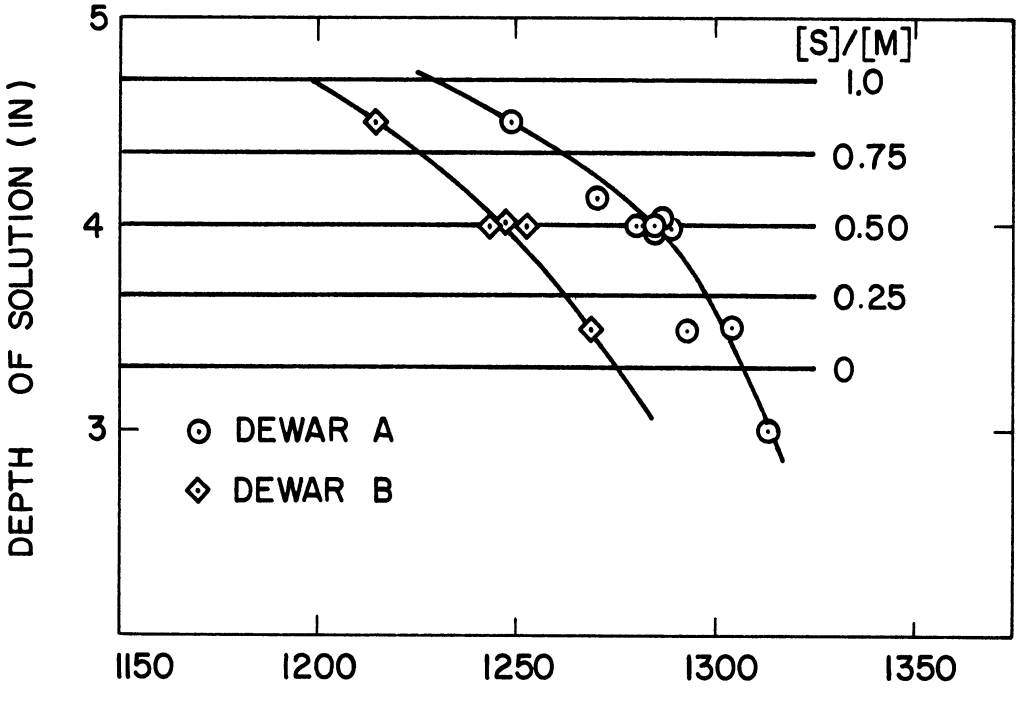


Figure IV-11. Dose Rate in PRF Source. Top - Dose Rate Outside of Center Well, on Mid-plane, North of Source. Bottom - Dose Rate in Dewar A and B in Center Well for Various Depths of Solution in Reaction Tubes.

V DISCUSSION OF RESULTS

A. Derivation of Equations

1. Introduction

Equations for the free radical copolymerization of styrene and sulfur dioxide were derived by Barb.(5,6,7) He found a minimum styrene to sulfur dioxide ratio of 2:1 in polymers prepared at 20°C and above and accounted for this by assuming copolymerization of styrene with a 1:1 styrene/sulfur dioxide complex. The existence of such a complex was confirmed by ultraviolet spectroscopy.(5) At 0°C and -20°C Barb obtained polymers with styrene/sulfur dioxide ratios of less than 2:1 and assumed the involvement, at these temperatures, of a reaction between a complexyl radical and another molecule of the 1:1 complex.

In an analysis of Barb's work, Walling(115) showed that it is unnecessary to assume the involvement of a complex in order to explain the kinetics of the reaction; the observed behavior can result directly from the reversibility of the copolymerization reaction and it is not possible to distinguish kinetically between the two processes. Furthermore, since Barb's experimental results lead to the requirement that the equilibrium constant for complex formation be small, his reaction scheme leads to the dubious conclusion that molecular sulfur dioxide has negligible reactivity with the growing polymer chain compared to the reactivity of the complex. For these reasons and in accordance with the principle that it is generally unwise to introduce unnecessary assumptions, the kinetic scheme proposed by Walling will be used in preference to that of Barb.

In the remaining discussion, the following notation will be used. It is essentially the notation used by Walling. Where different, the notation of Barb is given in parentheses.

M	Styrene	
S	Sulfur Dioxide	(Sd)
$M\cdot$	Polymer radical ending in -M-M·	$(M\cdot_j)$
$M\cdot'$	Polymer radical ending in -M-S-M·	$(C\cdot_j)$
$S\cdot$	Polymer radical ending in -M-M-S·	$(Sd\cdot_{j-1})$
$S\cdot'$	Polymer radical ending in -S-M-S·	$(Sd\cdot_{j-1})$
[M], [S]	concentration, moles/liter	
C	complex of M + S (in Barb's scheme)	
P	dead polymer	
k	propagation (or depropagation) rate constant	
k_i	initiation rate constant	
k_t	termination rate constant	
K	equilibrium constant for complex formation	
r_1, r_3	ratios of rate constants	
p_1, p_2, p_3	ratios of rate constants	
R_i	initiation rate	
R_t	termination rate	
I	radiation intensity, rad/min	
n	molar ratio of M to S in polymer	
t	time, min	

Note: Subscripts denoting chain length will be omitted.

In the following analysis the usual steady state assumption will be used - i.e., the concentration of each type of free radical remains constant throughout the reaction. It will also be assumed that the rate constants do not change with the length of the growing polymer chain.

The postulated free radical chain reaction mechanism is as follows:

Initiation ($R_i = I\ k_i$) (1)

$M \rightarrow M\cdot$		(2)
$S \rightarrow S\cdot$		(3)

Propagation

	$M\cdot + M \rightarrow M\cdot$	k_{11}	(4)
	$M\cdot + S \rightleftarrows S\cdot$	k_{12}, k_{-12}	(5)
	$S\cdot + M \rightleftarrows M\cdot'$	k_{21}, k_{-21}	(6)
	$M\cdot' + M \rightarrow M\cdot$	$k_{31} = k_{11}$	(7)
at low temperatures only	$M\cdot' + S \rightleftarrows S\cdot'$	k_{32}, k_{-32}	(8)
	$S\cdot' + M \rightleftarrows M\cdot'$	k_{21}, k_{-21}	(9)

Depropagation

	$S\cdot \rightleftarrows M\cdot + S$	k_{-12}, k_{12}	(5)
	$M\cdot' \rightleftarrows S\cdot + M$	k_{-21}, k_{21}	(6)
(low temp.)	$S\cdot' \rightleftarrows M\cdot' + S$	k_{-32}, k_{32}	(8)

Termination

($M\cdot = M\cdot$ or $M\cdot'$, $S\cdot = S\cdot$ or $S\cdot'$)

$M\cdot + M\cdot \rightarrow P$	$k_{t\ MM}$	(10)
$S\cdot + M\cdot \rightarrow P$	$k_{t\ SM}$	(11)
$S\cdot + S\cdot \rightarrow P$	$k_{t\ SS}$	(12)

The following ratios will be used later:

$$r_1 = k_{11}/k_{12},\ r_3 = k_{31}/k_{32}$$

$$p_1 = k_{-12}/k_{21},\ p_2 = k_{-21}/k_{11},\ p_3 = k_{-32}/k_{21}$$

Some special features of these reactions may be noted:

a. If the kinetic chain length is long, the overall reaction rate is unaffected by the relative number of primary M· and S· radicals so that only the overall k_i for the initiation of M· plus S· radicals is needed.

b. Sulfur dioxide does not add to a S· type radical.

c. A chain with sulfur dioxide in the penultimate position (-M-S-M·) does not readily add sulfur dioxide - i.e., k_{32} is much smaller than k_{21}. There is no such effect on the addition of styrene however, so that $k_{31} = k_{11}$ and reaction (9) has the same rate constants as (6).

d. Depropagation can occur only at -M-S· (or -S-M·) bonds so that reactions (5), (6) and (8) are reversible but not (4) and (7).

e. Reactions (8) and (9) should occur only at low temperatures where polymers containing less than two moles of styrene per mole of sulfur dioxide ($n < 2$) are obtained. At these temperatures, k_{-21} will be assumed to be negligible ($p_2 = 0$).

Since a rate equation which accounts for all of the postulated reactions would be extremely cumbersome, more limited equations covering restricted temperature ranges will be derived. The restrictive assumptions will be the same as those used by Barb and found to agree with his results. The equations will be divided into a low temperature and a high temperature group:

Low temperature - No depropagation of M· or M·' ($k_{-21} = 0$). Concentration of S· is small enough for termination reactions (11) and (12) to be neglected.

High temperature - S does not add to $M\cdot'$ radicals so that reactions (8) and (9) can be neglected. Termination reactions (11) and (12) can be neglected in the lower temperatures of this range but they become significant as the concentration of $S\cdot$ radicals increases due to the increasing reversibility of reaction (6) at higher temperatures.

2. Composition Equations

a. Low Temperature

The following reactions are involved:

$$M\cdot + M \rightarrow M\cdot \qquad k_{11} \tag{4}$$

$$M\cdot + S \rightleftarrows S\cdot \qquad k_{12},\ k_{-12} \tag{5}$$

$$S\cdot + M \rightarrow M\cdot' \qquad k_{21}\ (k_{-21} = 0) \tag{6}$$

$$M\cdot' + M \rightarrow M\cdot \qquad k_{11} \tag{7}$$

$$M\cdot' + S \rightleftarrows S\cdot' \qquad k_{32},\ k_{-32} \tag{8}$$

$$S\cdot' + M \rightarrow M\cdot' \qquad k_{21}\ (k_{-21} = 0) \tag{9}$$

The rates of reaction of styrene and sulfur dioxide are:

$$-d[M]/dt = k_{11}\,[M]\,([M\cdot] + [M\cdot']) + k_{21}\,[M]\,([S\cdot] + [S\cdot']) \tag{13}$$

$$-d[S]/dt = k_{12}\,[S][M\cdot] + k_{32}\,[S][M\cdot'] - k_{-12}\,[S\cdot] - k_{-32}\,[S\cdot'] \tag{14}$$

From the steady state approximation, the rate of destruction of each radical species equals its rate of production so that:

$$k_{12}\,[M\cdot][S] = k_{-12}\,[S\cdot] + k_{11}\,[M\cdot'][M] \tag{15}$$

$$k_{21}\,[S\cdot][M] + k_{-12}\,[S\cdot] = k_{12}\,[M\cdot][S] \tag{16}$$

$$k_{11}\,[M\cdot'][M] + k_{32}\,[M\cdot'][S] = k_{21}\,[M]([S\cdot] + [S\cdot']) + k_{-32}\,[S\cdot'] \tag{17}$$

$$k_{21}\,[S\cdot'][M] + k_{-32}\,[S\cdot'] = k_{32}\,[M\cdot'][S] \tag{18}$$

Initiation and termination are ignored here since at steady state $R_i = R_t$ and there is no net effect on the relative concentrations of the various radicals.

Rewriting (16)

$$[M\cdot] = \frac{[S\cdot]\,(k_{21}\,[M] + k_{-12})}{k_{12}\,[S]} \tag{19}$$

equating (15) and (16)

$$[M\cdot'] = [S\cdot]\,k_{21}/k_{11} \tag{20}$$

which substituted in (18) gives

$$[S\cdot'] = \frac{[S\cdot][S]\,k_{21}\,k_{32}}{k_{11}\,(k_{21}\,[M] + k_{-32})} \tag{21}$$

Substuting for $M\cdot$, $M\cdot'$ and $S\cdot'$ in (13) and (14)

$$\frac{-d\,[M]}{dt} = k_{21}\,[M][S\cdot]\left[\frac{k_{11}}{k_{12}\,[S]}\left([M] + \frac{k_{-12}}{k_{21}}\right) + \frac{k_{21}\,k_{32}\,[S]}{k_{31}\,(k_{21}\,[M] + k_{-32})} + 2\right] \tag{22}$$

and

$$\frac{-d\,[S]}{dt} = k_{21}\,[S\cdot]\left[[M] + \frac{k_{32}}{k_{11}}\,[S] - \frac{k_{32}\,k_{-32}\,[S]}{k_{11}\,(k_{21}\,[M] + k_{-32})}\right] \tag{23}$$

Substituting $r_1 = k_{11}/k_{12}$, $r_3 = k_{11}/k_{32}$, $p_1 = k_{-12}/k_{21}$, $p_3 = k_{32}/k_{21}$

$$\frac{-d\,[M]}{dt} = k\quad[M][S\cdot]\left[\frac{r_1}{[S]}\,([M] + p_1) + \frac{[S]}{r_3\,([M] + p_3)} + 2\right] \tag{24}$$

and

$$\frac{-d\,[S]}{dt} = k_{21}\,[S\cdot][M]\left[1 + \frac{[S]}{r_3\,([M] + p_3)}\right] \tag{25}$$

Dividing (24) by (25)

$$n = \frac{d[M]}{d[S]} = \frac{[M]\left[\frac{r_1}{[S]}\left([M] + p_1\right) + \frac{[S]}{r_3\left([M] + p_3\right)} + 2\right]}{[M] + \frac{[S]}{r_3} + \frac{p_3\,[S]}{r_3\left([M] + p_3\right)}} \tag{26}$$

which reduces to

$$n-1 = \frac{(r_1p_1 + r_1\,[M] + [S])(r_3p_3 + r_3\,[M])}{[S]\,(r_3p_3 + r_3\,[M] + [S])} \tag{27}$$

b. <u>High Temperature</u>

The following reactions are involved:

$M\cdot + M \rightarrow M\cdot$ $\qquad k_{11}$ $\qquad$ (4)

$M\cdot + S \rightleftarrows S\cdot$ $\qquad k_{12},\ k_{-12}$ $\qquad$ (5)

$S\cdot + M \rightleftarrows M\cdot'$ $\qquad k_{21},\ k_{-21}$ $\qquad$ (6)

$M\cdot' + M \rightarrow M\cdot$ $\qquad k_{11}$ $\qquad$ (7)

The reaction rates for M and S are

$$-d\,[M]/dt = k_{11}\,[M]\,([M\cdot] + [M\cdot']) + k_{21}\,[M][S\cdot] - k_{-21}\,[M\cdot'] \tag{28}$$

$$-d\,[S]/dt = k_{12}\,[S]\,[M\cdot] - k_{-12}\,[S\cdot] \tag{29}$$

and at steady state

$$k_{12}\,[M\cdot]\,[S] = k_{-12}\,[S\cdot] + k_{11}\,[M\cdot']\,[M] \tag{30}$$

$$k_{21}\,[S\cdot]\,[M] + k_{-12}\,[S\cdot] = k_{12}\,[M\cdot]\,[S] + k_{-21}\,[M\cdot'] \tag{31}$$

$$k_{11}\,[M\cdot']\,[M] + k_{-21}\,[M\cdot'] = k_{21}\,[S\cdot]\,[M] \tag{32}$$

Rewriting (32)

$$[M\cdot'] = \frac{k_{21}\,[M]\,[S\cdot]}{k_{31}\,[M] + k_{-21}} \tag{33}$$

which substituted in (3) gives

$$[M\cdot] = \frac{[S\cdot]}{k_{12}\,[S]}\left[k_{-12} + \frac{k_{11}\,k_{21}\,[M]^2}{k_{31}\,[M] + k_{-21}}\right] \tag{34}$$

Substituting (33) and (34) in (28) and (29)

$$\frac{-d\,[M]}{dt} = k_{21}\,[M]\,[S\cdot]\left[\frac{k_{11}}{k_{12}\,[S]}\left(\frac{k_{-12}}{k_{21}} + \frac{k_{11}\,[M]^2}{k_{11}\,[M] + k_{-21}}\right) + \frac{k_{11}\,[M]}{k_{11}\,[M] + k_{-21}} + 1 - \frac{k_{-21}}{k_{11}\,[M] + k_{-21}}\right] \tag{35}$$

and

$$\frac{-d\,[S]}{dt} = k_{21}\,[M]\,[S\cdot]\;\frac{k_{11}\,[M]}{k_{11}\,[M] + k_{-21}} \tag{36}$$

Substituting $r_1 = k_{11}/k_{12}$, $p_1 = k_{-12}/k_{21}$, $p_2 = k_{-21}/k_{11}$

$$\frac{-d\,[M]}{dt} = k_{21}\,[M]\,[S\cdot]\left[\frac{r_1}{[S]}\left(p_1 + \frac{[M]^2}{[M] + p_2}\right) + \frac{[M]}{[M] + p_2} + 1 - \frac{p_2}{[M] + p_2}\right] \tag{37}$$

and

$$\frac{-d\,[S]}{dt} = k_{21}\,[M]\,[S\cdot]\;\frac{[M]}{[M] + p_2} \tag{38}$$

Dividing (37) and (38)

$$n = \frac{d\,[M]}{d\,[S]} = \frac{\frac{r_1}{[S]}\left(p_1 + \frac{[M]^2}{[M] + p_2}\right) + \frac{[M]}{[M] + p_2} + 1 - \frac{p_2}{[M] + p_2}}{\frac{[M]}{[M] - p_2}} \tag{39}$$

which reduces to

$$n - 2 = \frac{r_1 p_1}{[S]}\left[1 + \frac{p_2}{[M]} + \frac{[M]}{p_1}\right] \tag{40}$$

3. Reaction Rate Equations

a. Low Temperatures

As states previously, it is assumed that at lower temperatures there is negligible S· involvement in termination. Accordingly at steady state:

$$R_i = k_i I = R_t = k_{t\ MM} ([M\cdot] + [M\cdot'])^2 \qquad (41)$$

Substituting (19) and (20) for $[M\cdot]$ and $[M\cdot']$

$$k_i I = k_{t\ MM} [S\cdot]^2 k_{21}^2 \left[\frac{1}{k_{11}} + \frac{[M] + k_{-21}/k_{21}}{k_{12}\ [S]}\right]^2$$

and using $r_1 = k_{11}/k_{12}$ and $p_1 = k_{-12}/k_{21}$

$$k_i I = (k_{21}\ [S\cdot])^2 k_{t\ MM} \left[\frac{[S] + r_1\ [M] + r_1 p_1}{k_{11}\ [S]}\right]^2$$

or

$$k_{21}\ [S\cdot] = (I\ k_i/k_{t\ MM})^{1/2} \frac{k_{11}\ [S]}{[S] + r_1\ [M] + r_1 p_1} \qquad (42)$$

The equation for the reaction rate of S has been derived previously:

$$\frac{-d\ [S]}{dt} = k_{21}\ [S\cdot]\ [M] \left[1 + \frac{[S]}{r_3\ ([M] + p_3)}\right] \qquad (25)$$

Equating (24) with (42)

$$\frac{-d\ [S]}{dt} = (I\ k_i/k_{t\ MM})^{1/2} k_{11}\ [M] \left[1 + \frac{[S]}{r_3\ ([M] + p_3)}\right]\left[\frac{[S]}{[S] + r_1\ [M] + r_1 p_1}\right] \qquad (43)$$

b. <u>High Temperatures</u>

If the same termination assumption is made as in (a):

$$k_i I + k_{t\ MM} ([M\cdot] + [M\cdot'])^2 \qquad (41)$$

Substituting (33) and (34) for $[M\cdot]$ and $[M\cdot']$ and using $r_1 = k_{11}/k_{12}$, $p_1 = k_{-12}/k_{21}$, $p_2 = k_{-21}/k_{11}$

$$k_i I = k_{t\ MM} \left[\frac{k_{21}\ [M]\ [S\cdot]}{k_{11}\ [S]} \frac{[S] + r_1 p_1 + r_1\ [M] + r_1 p_1 p_2/[M]}{[M] + p_2}\right]^2 \qquad (44)$$

or

$$k_{21}\,[M]\,[S\cdot] = (k_i I/k_{t\ MM})^{1/2}\,\frac{k_{11}\,[S]\,([M] + p_2)}{[S] + r_1p_1 + r_1\,[M] + r_1p_1p_2/[M]} \qquad (45)$$

Using the previously derived equation for the reaction rate of S,

$$\frac{-d\,[S]}{dt} + k_{21}\,[M]\,[S\cdot]\;\frac{[M]}{[M] + p_2} \qquad (38)$$

Combining (38) and (43)

$$\frac{-d\,[S]}{dt} = (I\,k_i/k_{t\ MM})^{1/2}\,\frac{k_{11}\,[S]\,[M]}{[S] + r_1p_1 + r_1\,[M] + r_1p_1p_2/[M]} \qquad (46)$$

or

$$\frac{1}{-d\,[S]/dt} = \left[\frac{k_{t\ MM}}{I\,k_i}\right]^{1/2}\frac{1}{k_{11}\,[M]}\left[\frac{r_1[M]}{[S]} + \frac{r_1p_1}{[S]}\left(1 + \frac{p_2}{[M]}\right) + 1\right] \qquad (46a)$$

If all three termination reactions are considered*

$$k_iI = k_{t\ MM}\,([M\cdot] + [M\cdot']) + 2\,k_{t\ SM}\,[S\cdot]\,([M\cdot] + [M\cdot']) + k_{t\ SS}\,[S\cdot]^2 \qquad (47)$$

and from (42)

$$[M\cdot] + [M\cdot'] = [S\cdot]\left[\frac{k_{21}}{k_{11}}\,\frac{[M]}{[S]}\,\frac{[S] + r_1p_1 + r_1\,[M] + r_1p_1p_2/[M]}{[M] + p_2}\right]$$

Calling the terms in the brackets A

$$[S\cdot] = (k_iI)^{1/2}\,(k_{t\ MM}\,A^2 + 2\,k_{t\ SM}\,A + k_{t\ SS})^{-1/2} \qquad (48)$$

and substituting for [S.] in (38)

$$\frac{-d\,[S]}{dt} = (k_iI)^{1/2}\,k_{21}\,\frac{[M]^2}{[M] + p_2}\left[k_{t\ MM}\,A^2 + 2\,k_{t\ SM}\,A + k_{t\ SS}\right]^{-1/2} \qquad (49)$$

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* The notation for the k_t's is the same as that used by Barb but differs from that of Flory$^{(44)}$ who uses a 2 before each k_t to denote the consumption of two radicals. The 2 $k_{t\ MS}$ here is based on the collision frequency **rate** which is twice as great for cross termination.

where

$$A = \frac{k_{21}}{k_{11}} \frac{[M]}{[S]} \frac{[S] + r_1 p_1 + r_1 [M] + r_1 p_1 p_2/[M]}{[M] + p_2}$$

Equation (49) can be greatly simplified if $k_{t\ SM} = (k_{t\ MM}\, k_{t\ SS})^{1/2}$. This relationship usually does not hold in copolymerizations but Barb(7) has shown that the resulting equation nevertheless holds over his experimental range. This simplification, therefore, will be tried here.

Assuming the above relationship, (49) becomes

$$\frac{-d\,[S]}{dt} = \left[\frac{k_i I}{k_{t\ MM}}\right]^{1/2} k_{21} \frac{[M]^2}{[M] + p_2} \left[A + \frac{k_{t\ SM}}{k_{t\ MM}}\right]^{-1} \tag{50}$$

or

$$\frac{-1}{d\,[S]/dt} = \frac{\dfrac{k_{21}}{k_{11}} \dfrac{[M]}{[S]} \dfrac{[S] + r_1 [M] + r_1 p_1 (1 + p_2/[M])}{[M] + p_2} + \dfrac{k_{t\ SM}}{k_{t\ MM}}}{(I\, k_i/k_{t\ MM})^{1/2}\, k_{21}\, [M]^2/(M + p_2)} \tag{51}$$

which reduces to

$$\frac{-1}{d\,[S]/dt} = \left[\frac{k_{t\ MM}}{I\, k_i}\right]^{1/2} \frac{1}{k_{11}\,[M]} \left[\frac{r_1\,[M]}{[S]} + \frac{r_1 p_1}{[S]}\left(1 + \frac{p_2}{[M]}\right) + 1 + \frac{k_{11}}{k_{21}} \frac{k_{t\ SM}}{k_{t\ MM}} \left(1 + \frac{p_2}{[M]}\right)\right] \tag{52}$$

which is the same as (46a) except for the added term in the brackets:

$$\frac{k_{11}}{k_{21}} \frac{k_{t\ SM}}{k_{t\ MM}} \left(1 + \frac{p_2}{[M]}\right)$$

4. Comparison with Equations of Barb

In this section the equations derived in the preceding sections will be compared with the equivalent expressions derived by Barb(5,6,7) on the basis of participation of a complex. Barb's experimental results will be used to simplify the equations to a more usable form by discarding the negligible terms. For this purpose his results are more suitable since Barb varied the concentration of styrene whereas in our work only undiluted styrene was used.

Table III compares the individual reactions of the two schemes. Equivalent reactions are, as far as possible, matched on the same line. Note that Barb assumes that the complex always adds to give a terminal structure of -S-M· and not -M-S· . In Barb's equations, k_{MM} will be used in place of k_{CM} in all cases.

a. Composition Equations

The composition equation derived from Barb's reaction scheme assuming no depropagation is

$$n-1 = \frac{1 + \frac{k_{MM}}{k_{MC}K} \frac{1}{[S]}}{1 + \frac{k_{CC}K}{k_{MM}} [S]} \tag{53}$$

At 0° C he obtained $k_{CC}K/k_{MM} = 0.09$ l./mole compared to approximately 50 l./mole for $k_{MC}K/k_{MM}$ and approximated this equation by (Reference 7, Equation (8))

$$\frac{1}{n-1} = 1 + \frac{k_{CC}K}{k_{MM}} [S] \tag{54}$$

At 20° C and above, k_{CC} was assumed negligible yielding (Reference 5, Equation (i))

$$n-2 = \frac{k_{MM}}{k_{MC}K} \frac{1}{[S]} \tag{55}$$

which was not independent of [M] below 4 m./l.

TABLE III

COMPARISON OF REACTION SCHEMES OF WALLING AND BARB

WALLING		BARB	
Propagation			
		$[C] = K\,[M]\,[S]$	
$M\cdot + M \rightarrow M\cdot$	k_{11}	$M\cdot + M \rightarrow M\cdot$	k_{MM}
$M\cdot + S \rightleftarrows S\cdot$	k_{12}	$M\cdot + C \rightarrow C\cdot$	k_{MC}
$S\cdot + M \rightleftarrows M\cdot'$	k_{21}	$S\cdot + M \rightleftarrows C\cdot$	k_{SM}
$M\cdot' + M \rightarrow M\cdot$	$k_{31} = k_{11}$	$C\cdot + M \rightarrow M\cdot$	$k_{CM} = k_{MM}$
Low Temperature only			
$M\cdot' + S \rightleftarrows S\cdot'$	k_{32}	$C\cdot + C \rightarrow C\cdot$	k_{CC}
$S\cdot' + M \rightarrow M\cdot'$	k_{21}		
$(k_{-21} = 0)$			
Depropagation			
$S\cdot \rightleftarrows M\cdot + S$	k_{-12}	$S\cdot \rightarrow M\cdot + S$	k_S
$M\cdot' \rightleftarrows S\cdot + M$	k_{-21}	$C\cdot \rightleftarrows S\cdot + M$	k_C
Low Temperature only			
$S\cdot' \rightleftarrows M\cdot' + S$	k_{-32}		
Termination			
$M\cdot = M\cdot$ or $M\cdot'$; $S\cdot = S\cdot$ or $S\cdot'$		$M\cdot = M\cdot$ or $C\cdot$	
$M\cdot + M\cdot \rightarrow P$	$k_{t\ MM}$	$M\cdot + M\cdot \rightarrow P$	$k_{t\ MM}$
$S\cdot + M\cdot \rightarrow P$	$k_{t\ SM}$	$S\cdot + M\cdot \rightarrow P$	$k_{t\ SM}$
$S\cdot + S\cdot \rightarrow P$	$k_{t\ SS}$	$S\cdot + S\cdot \rightarrow P$	$k_{t\ SS}$

Including depropagation reactions, Barb obtained

$$n-2 = \frac{k_{MM}}{k_{MC}K\ [S]}\left[1 + \frac{k_C\ k_S}{k_{MM}\ [M]\ (k_S + k_{SM}\ [M])}\right] \tag{56}$$

but since (n-2) [S] was found(5,7,115) to be a linear function of 1/[M] at both 20° and 60° C, $k_S \gg k_{SM}$ [M] and (56) becomes

$$n-2 = \frac{k_{MM}}{k_{MC}K\ [S]}\left[1 + \frac{k_C}{k_{MM}\ [M]}\right] \tag{57}$$

Rewriting Equation (40)

$$n-2 = \frac{r_1 p_1}{[S]}\left[1 + \frac{p_2}{[M]} + \frac{[M]}{p_1}\right] \tag{40}$$

and again assuming linearity with 1/[M] we have

$$n-2 = \frac{r_1 p_1}{[S]}\left[1 + \frac{p_2}{[M]}\right] \tag{58}$$

which is identical in form to (57) with

$$r_1 p_1 = k_{MM}/k_{MC}K \quad \text{and} \quad p_2 = k_C/k_{MM}$$

Walling(115) also notes that "the ratios k_C/k_{MM} and k_{-21}/k_{31} [M] refer to the same processes: the relative rates at which chains ending in -S-M· lose styrene or add an additional styrene unit. The quantities in front of the brackets are also similar. $k_{MM}/k_{MC}K$ is the monomer reactivity ratio for M and C with M·, taking into account the actual amount of complex present, while r_1p_1 is the monomer reactivity ratio for M and S with M·, adjusted for the fraction of M-S· which reverts to M· by loss of sulfur dioxide." Barb's data gives, at 60°, r_1p_1 = 1.0 mole/l and p_2 = 3.1 mole/l and at 20° r_1p_1 = 0.08 and p_2 = 0.9. Since p_1 must be very large (> 100 at 20°) for $[M]/p_1$ to be negligible in (40), r_1 must be very small.

The equivalent of Equation (54) for the composition at 0° C is

$$n-1 = \frac{(r_1p_1 + r_1\,[M] + [S])(r_3p_3 + r_3\,[M])}{[S]\,(r_3p_3 + r_3\,[M] + [S])} \tag{27}$$

and since r_1p_1 and r_1 would be even lower at 0° C than at 20° C, (27) becomes

$$\frac{1}{n-1} = 1 + \frac{[S]}{r_3p_3 + r_3\,[M]} \tag{59}$$

which would be the same as (54) if $r_3p_3 >> r_3\,[M]$. Since p_3 must be even greater than p_1 because of the closer proximity of the terminal-S· to the preceding sulfur dioxide unit and since Barb obtains a straight line with a slope of 0.09 l./mole at 0° C from a plot of 1/n-1 vs [S], it is evident that r_3 must be small, giving $k_{MM}/k_{CC}K = r_3p_3 = 11$ mole/l. for Barb's data. Equation (28) thus becomes

$$\frac{1}{n-1} = 1 + \frac{[S]}{r_3p_3} \tag{60}$$

b. Rate Equations

Barb's reaction scheme for low temperatures gives, for the reaction rate of sulfur dioxide,

$$\frac{-d\,[S]}{dt} = \left[\frac{R_i}{k_{t\ MM}}\right]^{1/2} k_{MM}\,[M]\,\frac{1 + \frac{k_{CC}K}{k_{MM}}\,[S]}{1 + \frac{k_{MM}}{k_{MC}K}\,\frac{1}{[S]}} \tag{61}$$

which, with the same simplification as in (54) becomes,

$$\frac{-d\,[S]}{dt} = \left[\frac{R_i}{k_{t\ MM}}\right]^{1/2} k_{MM}\,[M]\,\left[1 + \frac{k_{CC}K}{k_{MM}}\,[S]\right] \tag{62}$$

Eliminating the last term from Equation (43) by neglecting r_1 [M] + r_1p_1 as in the preceding discussion and ignoring r_3 [M] compared to r_3p_3, we get

$$\frac{-d\,[S]}{dt} = (I\ k_i/k_{t\ MM})^{1/2}\ k_{11}\ [M]\ \left[1 + \frac{[S]}{r_3p_3}\right] \tag{63}$$

which is identical to (62).

At higher temperatures, but ignoring $k_{t\ SM}$ and $k_{t\ SS}$, Barb obtains(7)

$$\frac{-1}{d\,[S]/dt} = \left[\frac{k_{t\ MM}}{R_i}\right]^{1/2} \frac{1}{k_{MM}\ [M]} \left[\frac{k_{MM}}{k_{MC}K\ [S]}\left(1 + \frac{k_C}{k_{MM}\ [M]}\right) + 1\right] \tag{64}$$

which is the same as (46a) if the r_1 [M]/[S] term is neglected as before, giving

$$\frac{-1}{d\,[S]/dt} = \left[\frac{k_{t\ MM}}{I\ k_i}\right]^{1/2} \frac{1}{k_{11}\ [M]} \left[\frac{r_1p_1}{[S]}\left(1 + \frac{p_2}{[M]}\right) + 1\right] \tag{65}$$

which is identical in form to (64).

Including $k_{t\ SM}$ and $k_{t\ SS}$ and assuming $k_{t\ SM} = (k_{t\ MM}\ k_{t\ SS})^{1/2}$ Barb obtains(7)

$$\frac{-1}{d\,[S]/dt} = \left[\frac{k_{t\ MM}}{R_i}\right]^{1/2} \frac{1}{k_{MM}\ [M]} \left[\frac{k_{MM}}{k_{MC}K\ [S]}\left(1 + \frac{k_C}{k_{MM}\ [M]}\right) + 1 + \frac{k_C\ k_{t\ SM}}{k_S\ k_{t\ MM}}\right] \tag{66}$$

which he writes in the form

$$\frac{-1}{d\,[S]/dt} = \left[\frac{k_{t\ MM}}{R_i}\right]^{1/2} \frac{1 + \alpha\ k_{MM}/Kk_{MC}\ \gamma\ [S]}{k_{MM}\ [M]/\gamma} \tag{66a}$$

where $\alpha = 1 + k_C/k_{MM}\ [M]$

and $\gamma = 1 + k_Ck_{t\ SM}/k_Sk_{t\ MM}$

The negligible terms in α and γ have been omitted. Equation (66) is similar in form to (52), the only difference being the lack of equivalence of the last term in the brackets:

$$\frac{k_{11}}{k_{21}} \frac{k_{t\ SM}}{k_{t\ MM}} \left(1 + \frac{p_2}{(M)}\right) \neq \frac{k_C}{k_S} \frac{k_{t\ SM}}{k_{t\ MM}} \tag{67}$$

This discrepancy is not surprising since while the two mechanisms are kinetically equivalent, they are not identical and, furthermore, the approximation $k_{t\ SM} = (k_{t\ MM}\, k_{t\ SS})^{1/2}$ is probably valid over only a limited range of compositions.

5. Summary of Simplified Forms

Composition Equations

Low Temperature

$$\frac{1}{n-1} = 1 + \frac{[S]}{r_3 p_3} \tag{60}$$

High Temperature

$$n-2 = \frac{r_1 p_1}{[S]} \left[1 + \frac{p_2}{[M]}\right] \tag{58}$$

Rate Equations

Low Temperature

$$\frac{-d\ [S]}{dt} = \left[\frac{I\ k_i}{k_{t\ MM}}\right]^{1/2} k_{11}\ [M] \left[1 + \frac{[S]}{r_3 p_3}\right] \tag{63}$$

or

$$\frac{-d\ [S]/dt}{[M]\ I^{1/2}} = \left[\frac{k_i}{k_{t\ MM}}\right]^{1/2} k_{11} \left[1 + \frac{[S]}{r_3 p_3}\right] \tag{63a}$$

High Temperature

assuming $k_{t\ MS} = k_{t\ SS} = 0$

$$\frac{-d\ [S]}{dt} = \left[\frac{I\ k_i}{k_{t\ MM}}\right]^{1/2} k_{11}\ [M] \left[\frac{1}{1 + \frac{r_1 p_1}{[S]}\left(1 + \frac{p_2}{[M]}\right)}\right] \qquad (65b)$$

or

$$\frac{-\ [M]\ I^{1/2}}{d\ [S]/dt} = \left[\frac{k_{t\ MM}}{k_i}\right]^{1/2} \frac{1}{k_{11}} \left[1 + \frac{r_1 p_1}{[S]}\left(1 + \frac{p_2}{[M]}\right)\right] \qquad (65a)$$

assuming $k_{t\ SM} = (k_{t\ MM}\ k_{t\ SS})^{1/2}$

$$\frac{-1}{d\ [S]/dt} = \left[\frac{k_{t\ MM}}{I\ k_i}\right]^{1/2} \frac{1}{k_{11}\ [M]} \left[1 + \left(1 + \frac{p_2}{[M]}\right)\left(\frac{r_1 p_1}{[S]} + \frac{k_{11}\ k_{t\ SM}}{k_{21}\ k_{t\ MM}}\right)\right] \qquad (68)$$

Rate of reaction of styrene

Since $-d[M]/dt = -(d\ [S]/dt)\ (d\ [M]/d\ [S]) = -\ n\ d\ [S]/dt$ the following equations can be obtained directly from the preceding relationships:

Low Temperature

$$\frac{-d\ [M]/dt}{[M]\ I^{1/2}} = \left[\frac{k_i}{k_{t\ MM}}\right]^{1/2} k_{11} \left[2 + \frac{[S]}{r_3 p_3}\right] \qquad (69)$$

High Temperature (assuming $k_{t\ MS} = k_{t\ SS} = 0$)

$$\frac{-d\ [M]/dt}{[M]\ I^{1/2}} = \left[\frac{k_i}{k_{t\ MM}}\right]^{1/2} k_{11} \left[1 + \frac{1}{1 + \frac{r_1 p_1}{[S]}\left(1 + \frac{p_2}{[M]}\right)}\right] \qquad (70)$$

These equations are invalid when $[S] = 0$ since Equation (19), used in the derivations, is indeterminate at $[S]$ and $[S\cdot]$ equal to zero. The correct equation for pure styrene is:

$$\frac{-d\ [M]/dt}{[M]\ I^{1/2}} = \left[\frac{k_i}{k_{t\ MM}}\right]^{1/2} k_{11} \qquad (70a)$$

In the foregoing discussion k_i has been treated as a constant. This is not quite true since there is no reason to believe that the same free radical yields should be obtained from styrene as from sulfur dioxide. In the simplest case where no energy transfer reactions occur k_i can be expressed as $k_{i\ M}\,[M] + k_{i\ S}\,[S]$. If energy transfer is considered, the situation becomes much more complex.(22)

B. Results at 0°C

The calculated results of the runs at 0° C and below are given in Table IV. The tabulated reactant compositions are the initial compositions except in those cases where either [S] or [M] changed by 2% or more during the reaction. In these cases, which are noted in the table, the mean values of [S] and [M] were used.

1. Reaction Rate

Figure V-1 shows the reaction rates at 0° C fitted to Equation (63a). A least squares fit to all points representing runs of 30 to 200 minutes (the reaction times over which the steady state assumption is justified) gives

$$\frac{-d\,[S]/dt}{[M]\,I^{1/2}} = 4.8 \times 10^{-7} \left[1 + \frac{[S]}{4.9}\right] \text{rad}^{-1/2}\ \text{min.}^{-1/2} \qquad (71)$$

giving $r_3p_3 = 4.9 \pm 0.5$ mole/l. and $k_{11}\,(k_i/k_{t\ MM})^{1/2} = (4.8 \pm 0.4) \times 10^{-7}$ (rad-min.)$^{-1/2}$ where the errors are the standard errors of the regression line.

The only points appreciably above this line are the two points representing Runs No. 185 and 222 which gave the two highest polymer yields at this temperature. Note that Run No. 185 which had a 3.3%

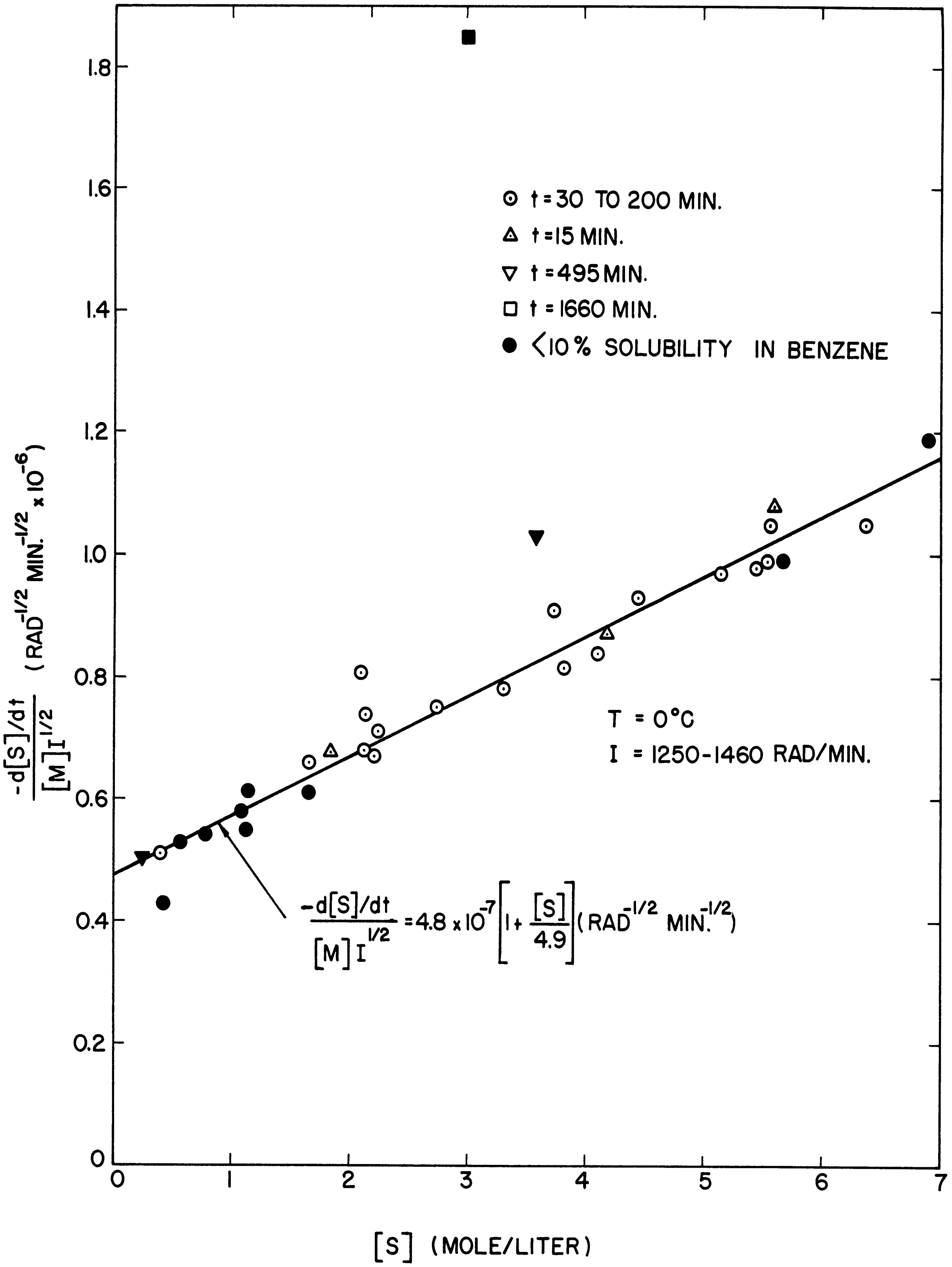

Figure V-1. Dependence of Reaction Rate of Sulfur Dioxide on Sulfur Dioxide Concentration. T = 0°C.

polymer yield shows a rate which is about 24% higher than expected whereas Run No. 222, having a 17% polymer yield shows a 140% increase in reaction rate. These results can be explained on the basis of the "gel effect" (Reference 9, p. 139), which results in a decrease in the rate of termination as the viscosity of the polymer solution increases. This effect is due to the diffusion controlled nature of the termination rate of the polymer radicals. As the solution thickens with additional polymer the high molecular weight radicals diffuse more slowly, thereby reducing the rate of termination and increasing both the reaction rate and the average molecular weight. The propagation rates are not seriously decreased because of the much faster diffusion of the low molecular weight monomers although the abnormally high sulfur content of No. 222 suggests some diffusion effect on styrene relative to sulfur dioxide. The gel effect is further intensified in these instances by the higher radiation level at the bottom of the reaction tubes since the polymers are denser than the monomer solutions.

2. Composition

Figure V-2 shows the results of fitting the composition data to Equation (60). The value, $r_3p_3 = 4.9$ from the rate data is shown as well as the value of $r_3p_3 = 11$ from the four composition values of Barb(7) (mostly at higher values of $[S]$). It can easily be seen that the data does not fit even though exactly the same assumptions were used in deriving Equation (60) as in Equation (63a).

Referring to Chapter IV we can see from Figure IV-9 that many of the 0° C polymers have rather high solubility in benzene even though

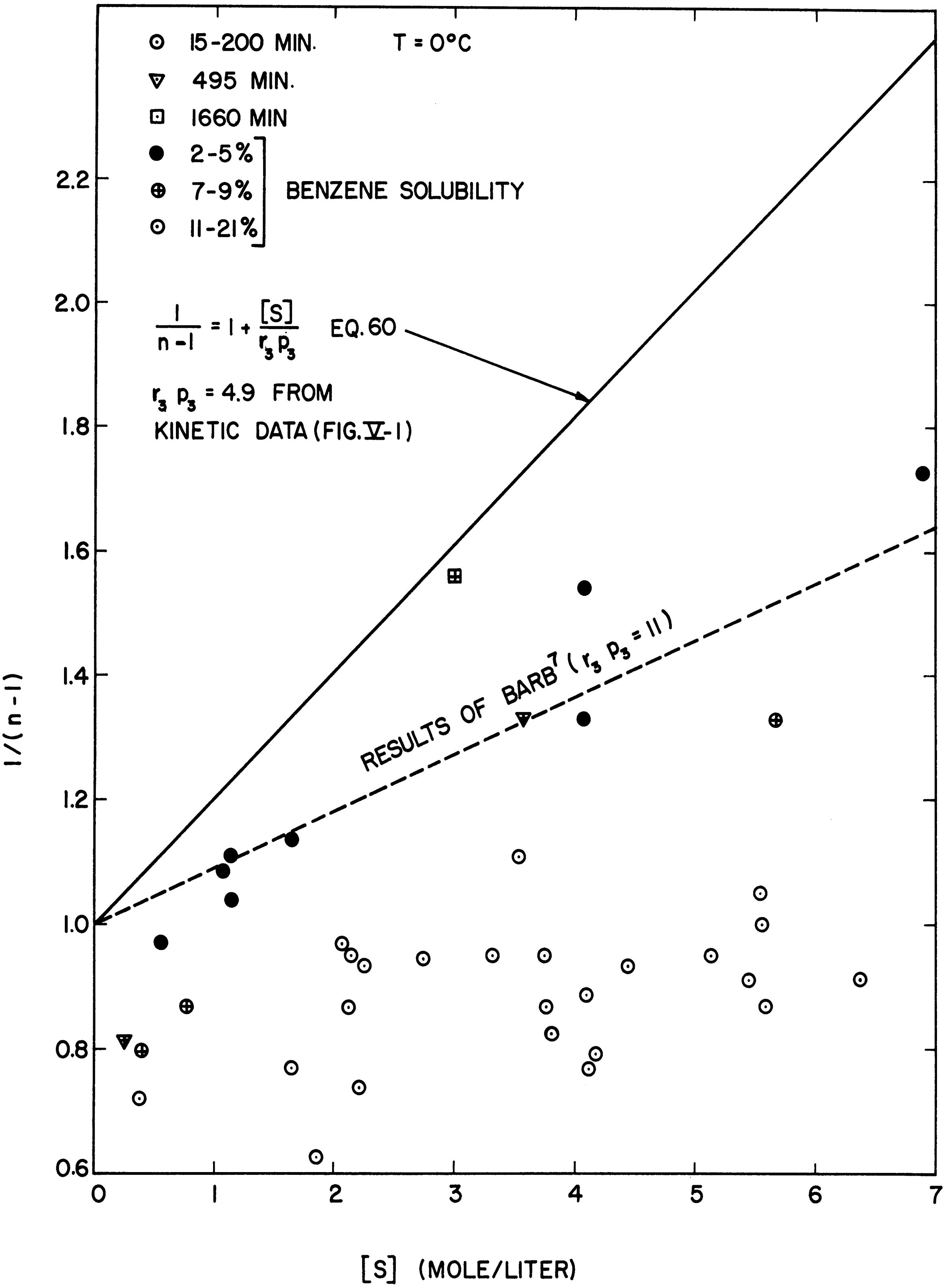

Figure V-2. Dependence of Polymer Composition on Sulfur Dioxide Concentration. T = 0°C.

some polymers of even lower sulfur content are substantially insoluble. Again referring to Figure V-2, we see that those polymers with minimum solubility in benzene come closest to following the slope of $r_3p_3 = 4.9$ and in fact do fit fairly well the line $r_3p_3 = 11$ of Barb. On the other hand those with over 10% solubility do not appear to increase in sulfur dioxide content at all with increasing $[S]$.

Why this effect does not show up in Figure V-1 can be seen in Figure V-3 which shows the rate function for styrene. Equation (71) is also plotted but only those points representing polymers of < 10% solubility accompany it. If the values from (71) are substituted in (69) the expected styrene reaction rate becomes

$$\frac{-d\,[M]/dt}{[M]\,I^{1/2}} = 4.8 \times 10^{-7} \left[2 + \frac{[S]}{4.9} \right] \tag{72}$$

which is also shown in Figure V-3. This equation, unlike that for the sulfur dioxide reaction rate, does not fit the data. In fact, the data appears to be best fitted by two lines as shown, one for the low solubility points (< 10%), the other for the high solubility points. Equation (71), conversely, while representing a least square fit of all the data, is seen here to fit the low solubility points equally well. From this information it appears that in addition to the postulated reaction, another reaction is taking place which does not appreciably interfere with the rate of sulfur dioxide consumption.

3. Analysis of Discrepancies

Barb(5) points out that at 20° C, reaction mixtures containing more than 50% by volume of sulfur dioxide and no free radical catalyst

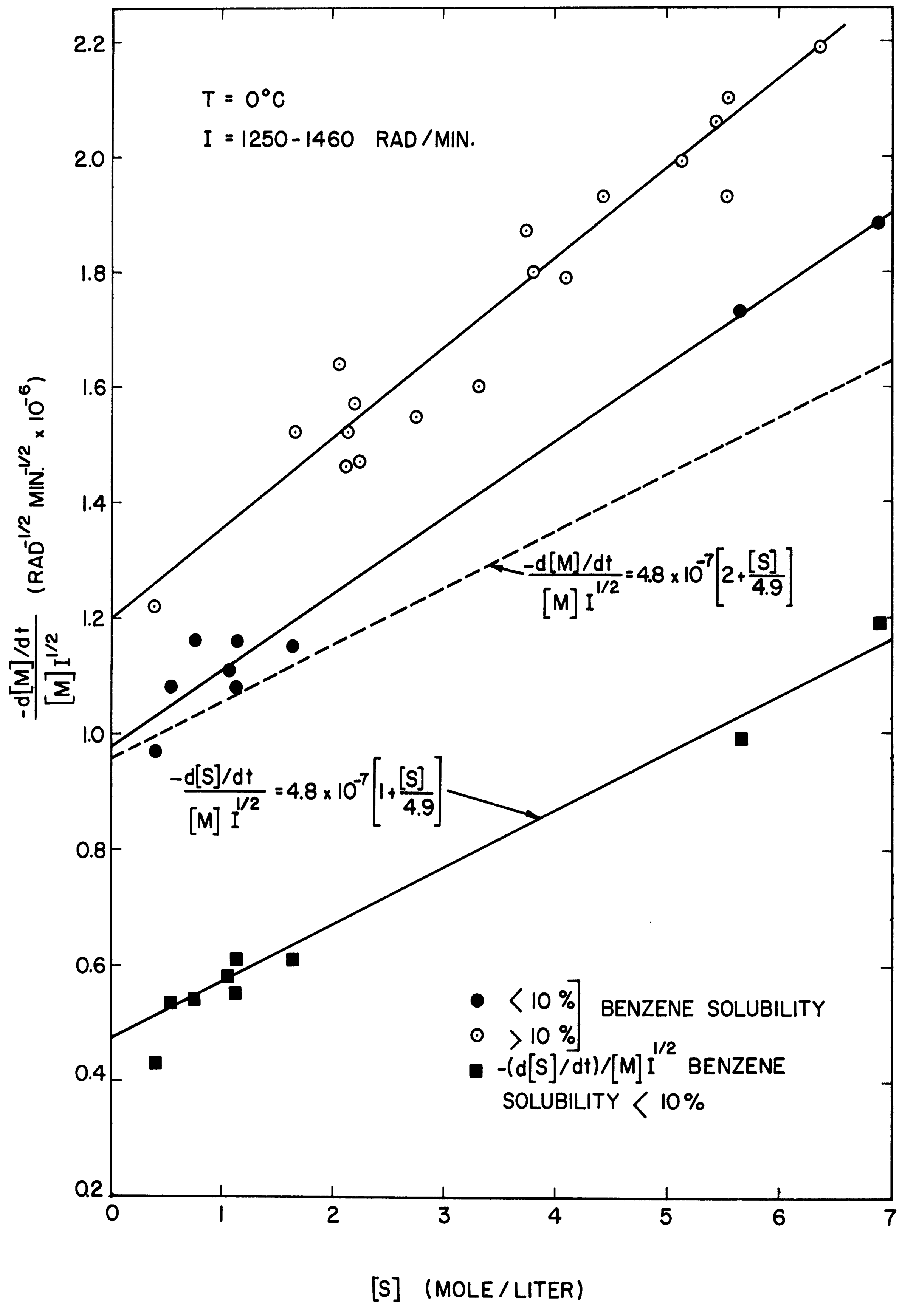

Figure V-3. Dependence of Reaction Rate of Styrene and Sulfur Dioxide Concentration. Curve and Low Solubility Points from Figure V-1 Included. T = 0°C.

produce polymers containing progressively less SO_2. He dissolved the polymers in benzene and analyzed the soluble and insoluble fractions separately obtaining $n = 2.05$ in the insoluble fraction and almost no sulfur in the soluble portion. When concentrated sulfuric acid was used as a cationic catalyst, almost pure polystyrene was obtained in solutions of 25% and 75% SO_2, whereas with a free radical catalyst, mixtures of these compositions gave n close to 2.

In an attempt to test this point, the values of n were recalculated on the assumption that the soluble fractions of the polymers contained pure polystyrene and that only the insoluble fractions, containing all of the sulfur dioxide, were involved in the free radical copolymerization. These values, called n_o, thus are the moles of styrene per mole of sulfur dioxide in the polymer assuming the weight of the polymer to be the insoluble fraction only.

These results are shown in Figure V-4 which is the same as Figure V-2 with n_o substituted for n. Again Equation (60) with $r_3p_3 = 4.9$ is shown and is seen to fit much of the data. The scatter of a number of points on the low side of this line can adequately be explained by the errors inherent in the solubility determination which were discussed in Chapter IV. Errors in sulfur determination are particularly apparent in this type of a plot. The possible magnitude of these errors is shown, using a reasonable assumption of error in sulfur content of $\pm$ 0.2% sulfur.

The phenomenon of a competing ionic and free radical radiation polymerization has been reported elsewhere. Chen and Stamm,(25) and Chen(26) were able to obtain simultaneous ionic and free radical

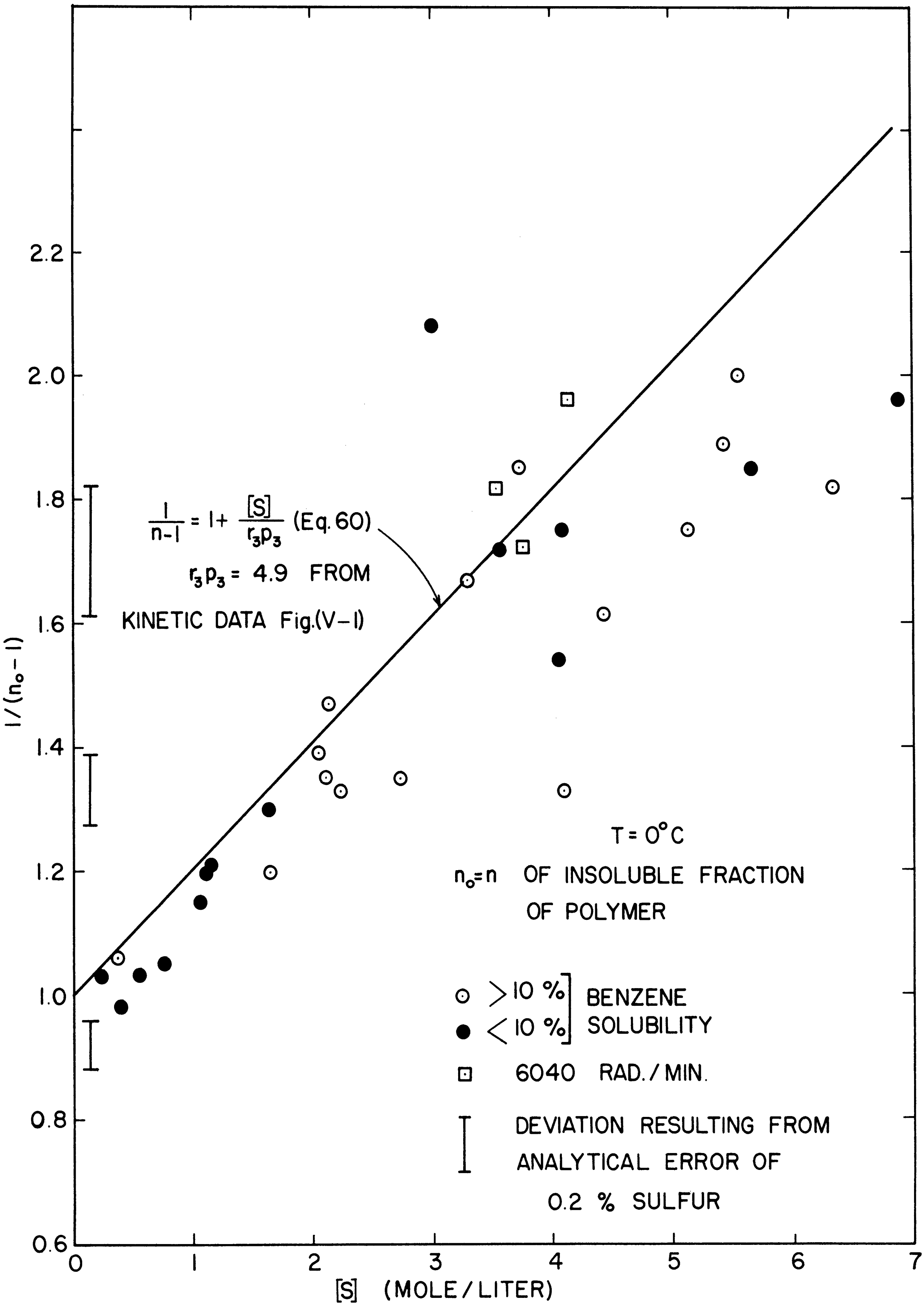

Figure V-4. Dependence of Insoluble Polymer Composition on Sulfur Dioxide Concentration. T = 0°C. n_o = n of Polymer Fraction Insoluble in Benzene, Assuming no SO_2 in Soluble Fraction.

polymerization of styrene in bulk and in methylene chloride solution at low temperatures with gamma radiation. The ionic mode showed a negative temperature coefficient and its rate was proportional to the first power of the radiation intensity. The rates of ionic and free radical polymerization were equal at about -15° C although this temperature increased with dose rate. Similar results were obtained by Chapiro and Stannett(23) for styrene in selected solvents. Two features of our data agree with these results. Figure IV-9 shows that of the three polymers prepared at 6040 rad/min., one has the highest solubility of any 0° C polymer and the other two are among the high solubility group. The two samples prepared at low dose rates both have very low solubilities. Also, abnormal solubility and abnormally high values of n are not noticeable above 10° C.

Since the side reaction does not occur to an appreciable extent in all cases, it is necessary to assume that it is influenced by some variable which was uncontrolled in the experiments.

If some of the tubes were not adequately degassed before adding sulfur dioxide, the irradiation could result in the oxidation of SO_2 to SO_3. Traces of water could result in small amounts of sulfurous and sulfuric acid. Since sulfuric acid is known to be a potent ionic catalyst for styrene polymerization, these factors could account for the observed phenomena. Figure V-5 showing the relationship between the solubility of the polymers and the concentration of sulfur dioxide in the reaction mixture shows that, in the case of the samples of more than 10% solubility, there is a noticeable increase in solubility with increasing sulfur dioxide concentration. This observation is consistent with the

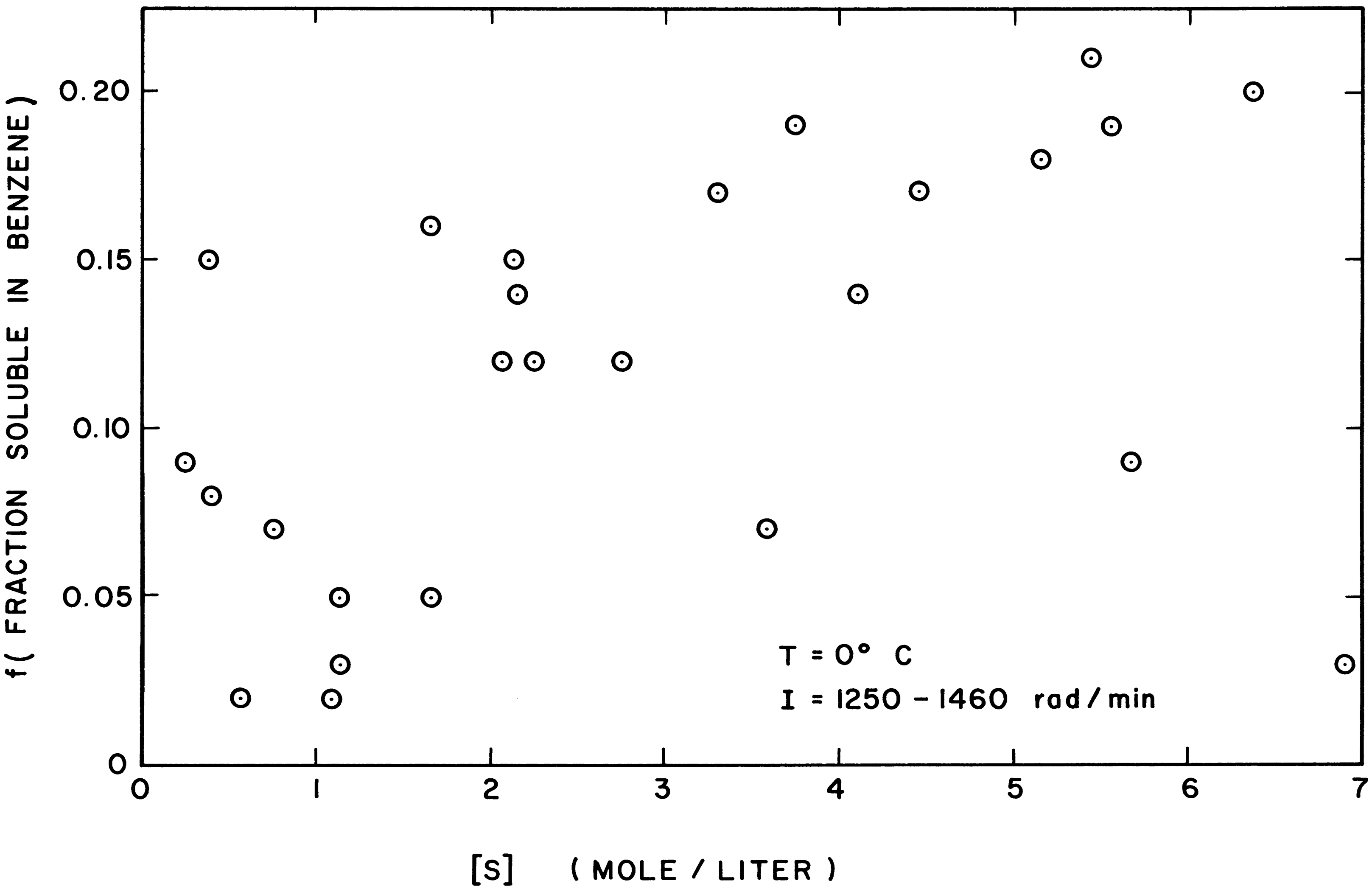

Figure V-5. Polymer Solubility in Benzene vs. Sulfur Dioxide Concentration at 1250-1460 rad/min. T = 0°C.

above explanation as well as with the results of Barb. Recently, Tokura(109) has conducted catalyzed cationic polymerization of styrene at -10° C in liquid sulfur dioxide which he found to be an excellent solvent for this purpose.

4. Rate Constants

Returning to Equation (71), additional information can be obtained by using the rate constants obtained for styrene polymerization by Matheson et al.(77) At 0° C, $k_{11} = 13.2$ l./mole-sec and $k_{t\ MM} = 3.32 \times 10^7$ l./mole-sec. (= 2 k_t in their notation) and become $k_{11} = 792$ l./mole-min. and $k_{t\ MM} = 1.99 \times 10^9$ l./mole-min. From Equation (71), $k_{11}\ (k_i/k_{t\ MM})^{1/2} = 4.8 \times 10^{-7}$ (rad-min)$^{-1/2}$ and substituting for k_{11} and $k_{t\ MM}$, $k_i = 7.3 \times 10^{-10}$ mole/l.-rad. From the relationship, 1 μ mole/l. = $963/\rho$ G rads (where ρ = density and G = chemical changes per 100 ev. absorbed) the G value for radical formation becomes (for $\rho = 1.02$): $G_R = 0.69$ radicals/100 ev.

Chapiro(22) calculated G_R values for styrene polymerization from all of the available data and obtained $G_R = 0.4$ at 1400 rad/min. The values increased to $G_R = 0.7$ below 60 rad/min. and decreased to $G_R = 0.35$ above 1800 rad/min. In calculating these values, Chapiro used values for $k_{t\ MM}/k_{11}^2$ obtained by Tobolsky and Offenbach(97) which are based on more recent results than those of Matheson et al. Individual values of k_{11} and $k_{t\ MM}$, however, were not obtained. At 0° C $k_{t\ MM}/k_{11}^2 = 1800$ moles/l.-min. giving $k_i = 4.14 \times 10^{-10}$ mole/l.-rad and $G_R = 0.39$, which is about 60% of the value obtained from the previous data. From this value of G_R it appears that the free radical yield in styrene-sulfur dioxide solutions is the same as in styrene alone.

The two pure styrene runs at 0° C (No. 160 and 161) do not, however, substantiate this claim. The average rate for the two experiments was

$$\frac{-d\,[M]/dt}{[M]\ I^{1/2}} = 7.1 \times 10^{-7}\ (\text{rad-min.})^{-1/2}$$

so from Equation (70a) $k_{11}\ (k_i/k_t)^{1/2} = 7.1 \times 10^{-7}$. Substituting for $k_{t\ MM}/k_{11}^{\ 2}$ as above, $k_i = 9.1 \times 10^{-10}$ and $G_R = 0.86$. The higher G_R value for pure styrene may indicate the presence of a simultaneous ionic reaction. Further evidence for this assumption will be given in the next section.

C. Variation of Temperature

The reaction rates of sulfur dioxide at the various temperatures are shown in Figures V-6 and V-7. Figure V-6 shows the low temperature data plotted to fit Equation (63a) and Figure V-7 shows the high temperature data fitted to Equation (65a). There is overlapping so that some of the data appear on both graphs. For the sake of clarity, the 60° and 64° data are omitted from the main scale of Figure V-7 and presented separately. Figure V-8 gives the reaction rates of styrene at all temperatures.

From these three graphs alone, it is not possible to tell where "low temperature" ends and "high temperature" begins. Data at 10°, 20° and 30° were not obtained over a wide enough range of sulfur dioxide concentrations to detect any curvature in these plots. But since from Equation (60) $1 < n < 2$ for the low temperature mechanism and from Equation (58) $n > 2$ at high temperatures, the dividing line

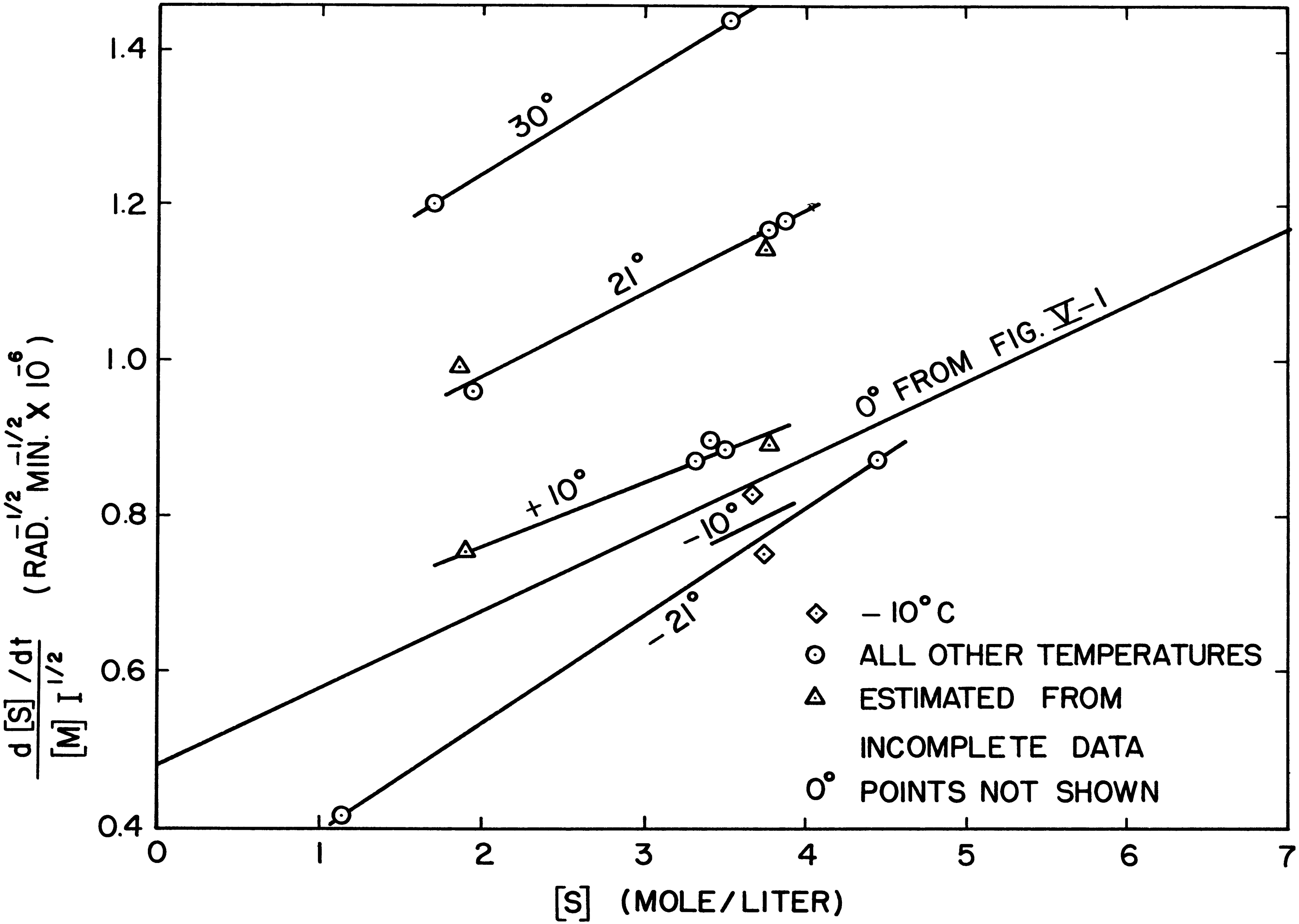

Figure V-6. Sulfur Dioxide Reaction Rates vs. Sulfur Dioxide Concentration at Low Temperatures.

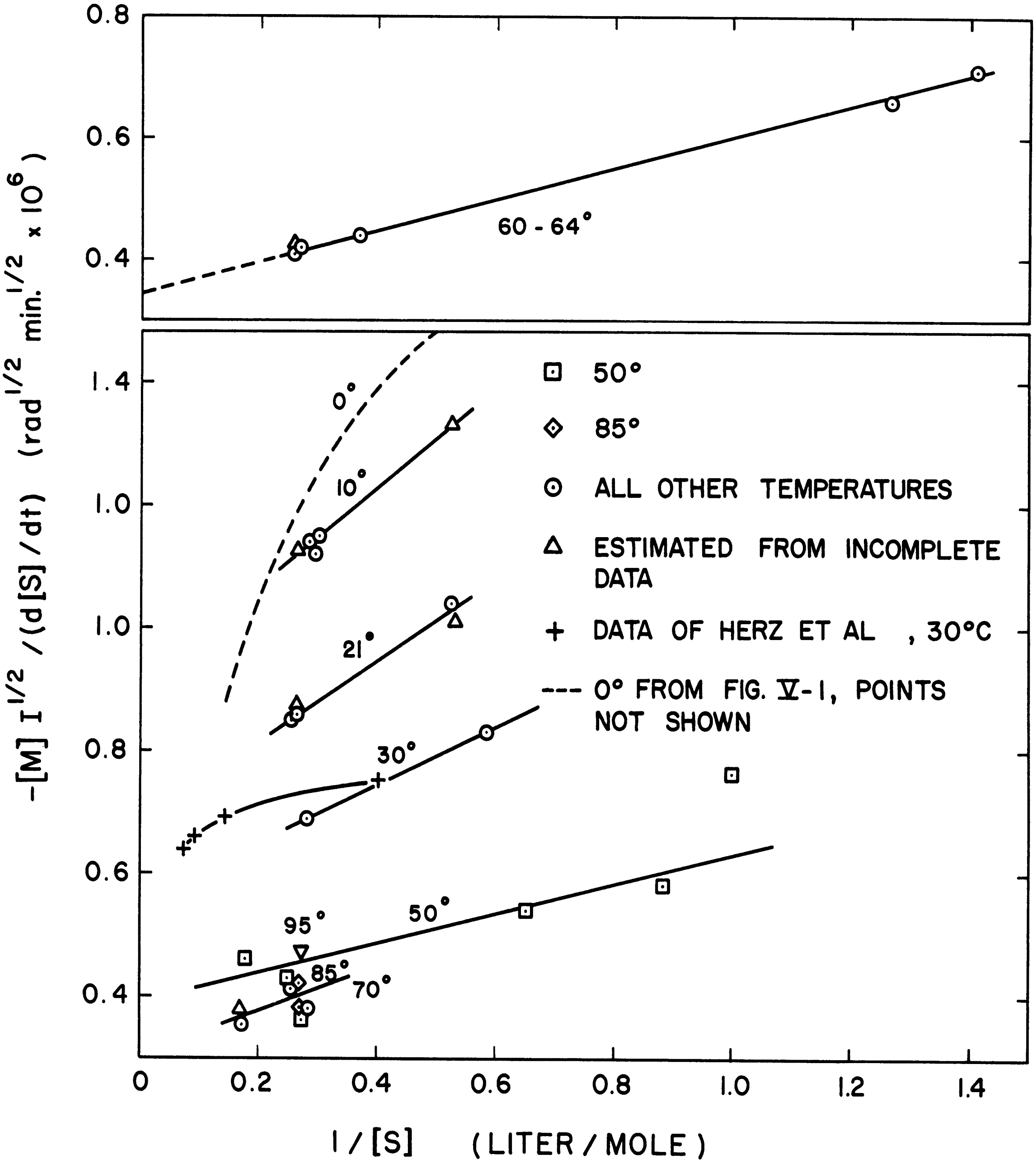

Figure V-7. Sulfur Dioxide Reaction Rates vs. 1/[S] at High Temperatures. Rate at 60°-64°C Shown Separately Above.

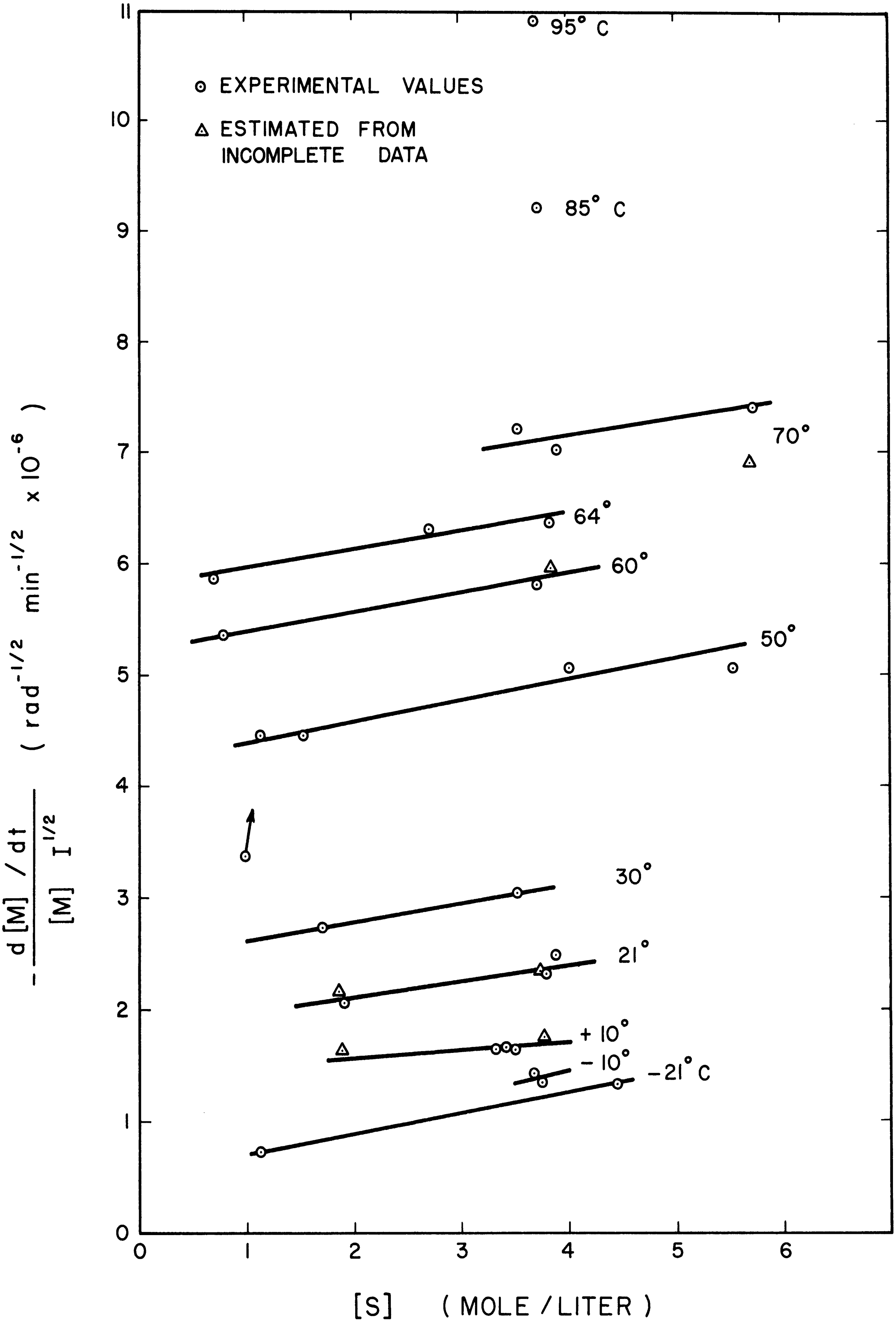

Figure V-8. Styrene Reaction Rates vs. Sulfur Dioxide Concentration.

would appear, from Tables IV and V, to be between 10° and 20°. Figure V-9, an Arrhenius plot for $[S] = 3.75$, indicates that this sharp division does in fact exist since there is an abrupt change in slope at about 10° C. The points on this plot represent interpolations from the previous three graphs. The 0° point on the styrene reaction rate curve is taken from the low solubility line in Figure V-3. The high solubility line clearly does not fit.

1. Composition Equations

The temperature dependence of polymer composition is shown in Arrhenius plots in Figures V-10 and V-12. The low temperature graph, Figure V-10, is based on Equation (60) $1/(n-1)=1+[S]/r_3p_3$ which can be rewritten as

$$\frac{1}{n-1} - 1 = \frac{2-n}{n-1} = \frac{[S]}{r_3p_3}$$

or

$$[S]\Big/\frac{2-n}{n-1} = r_3p_3. \tag{73}$$

From the Arrhenius equation, the activation energy E and frequency factor A for the propagation function r_3p_3 can be written as

$$r_3p_3 = A_{r_3p_3} \exp-(E_{r_3p_3}/RT) \tag{74}$$

or

$$\ln\left[[S]\ \frac{2-n}{n-1}\right] = -\ \frac{E_{r_3p_3}}{R}\,\frac{1}{T} + \ln A_{r_3p_3} \tag{75}$$

where T is in °K and the gas constant $R = 1.99$ calories/°C/mole. This equation is plotted in Figure V-10. In view of the evidence for

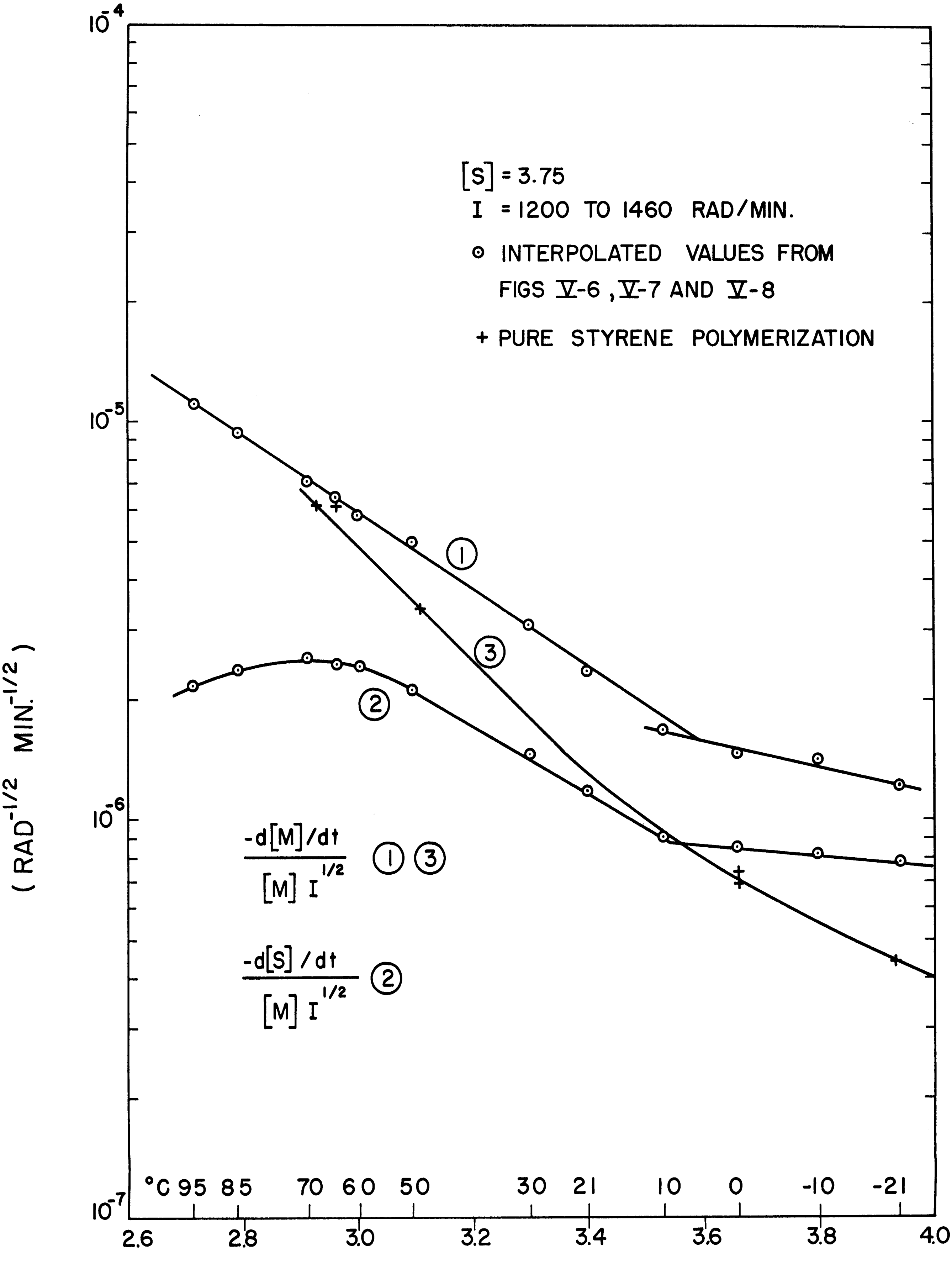

Figure V-9. Temperature Dependence of Reaction Rates of Styrene and of Sulfur Dioxide. Arrhenius Plot at [S] = 3.75. Interpolated from Figures V-6, V-7 and V-8.

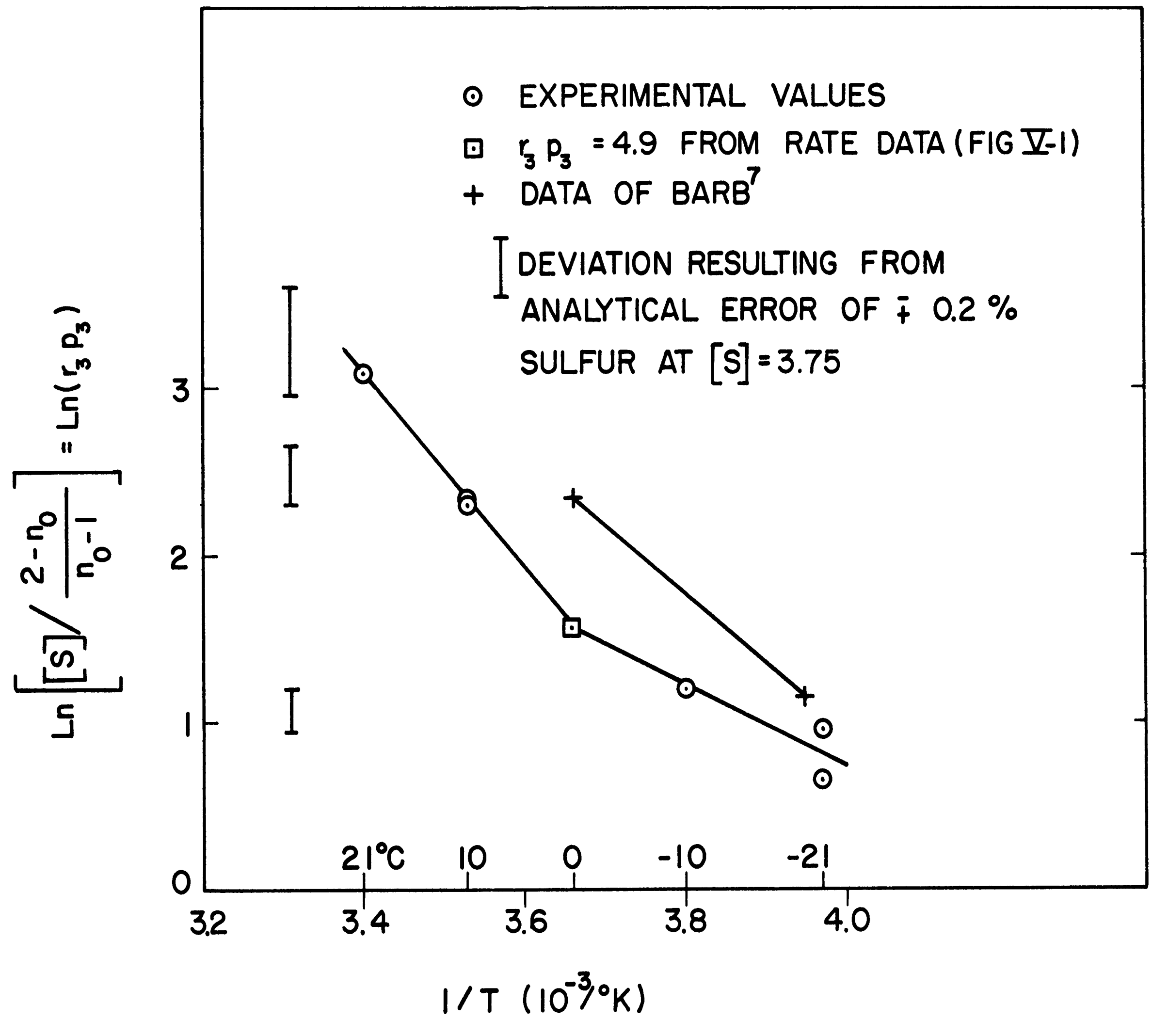

Figure V-10. Temperature Dependence of Polymer Composition - Low Temperatures.

simultaneous ionic polymerization at low temperatures, n_o, as defined in Part B, is used in place of n. The 0° C point is based on $r_3p_3 = 4.9$ moles/l. Unfortunately, solubility tests could not be run on all the low temperature polymers due to insufficient yield and some of the data at -10°, 10° and 21° C could not therefore be used in this plot.

A change in slope occurs at about 0°, giving $E_{r_3p_3} = 4.9$ kcal/mole below 0° and $E_{r_3p_3} = 12$ kcal./mole above 0°. Barb's data is also indicated. At these temperatures, Barb precipitated his polymers in benzene to avoid the polystyrene produced in any ionic side reaction. His 0° C data fit Equation (73) well, giving an average $r_3p_3 = 11$. At -20°C, however, r_3p_3 apparently increased from 3 at [S] = 5.3 to 16 at [S] = 15.1. This would indicate that at least at -20° the separation of polystyrene was not complete perhaps due to chain transfer between polysulfone radicals and "dead" polystyrene.(7) Even at 0°, his value of $r_3p_3 = 11$ is high compared to our value of 4.9 from kinetic data and may indicate incomplete separation of polystyrene in this case as well. Barb did not report any determination of the percentage of polystyrene produced.

In Figure V-10, there is no significance to the fact that the break point in the curve comes at 0°. The single 21° point represents the only sample of this temperature with an $n < 2$ and it is close enough to 2 so that it is subject to large errors in this type of a plot where the quantity $2-n$ is involved.

$E_{r_3p_3}$ can be written in terms of its components

$$E_{r_3p_3} = E_{11} + E_{-32} - E_{32} - E_{21} = 4.9 \text{ kcal}$$

Since Matheson et al.(77) have obtained from styrene polymerization $E_{11} = 7.8$ kcal,

$$E_{32} + E_{21} - E_{-32} = 3 \text{ kcal./mole} \tag{76}$$

The recent work of Herz, Hummel and Schneider(54,55) on the radiation copolymerization of styrene and sulfur dioxide covered temperatures from -78° to +30° C and sulfur dioxide concentrations generally above those used in this study.

At 30° C they obtained polymers with $n = 1.90$ to 2.08 for $[S]$ between 2.6 and 15.2. The one run in the present work which lies in this range, $[S] = 3.5$, gave $n = 2.1$ which is comparable. Above $[S] = 15.2$ (80 mole % SO_2) n increased due to ionic polymerization of styrene as had been previously reported by Barb.(5)

Using the analyses of Barb and Walling, Herz et al. derived simplified equations for high $[S]$, obtaining $n = 2$ and $-d[S]/dt = (I\, k_i/k_{t\ MM})^{1/2}\, k_{11}\, [M]$; for low temperatures they obtained Equation (54). Their limited rate data is plotted as a dotted line in Figure V-7, showing good agreement with this data for the one point in the same range. From their 30° C data, the authors calculated G_R values and noted that the free radical yield is almost independent of $[S]/[M]$ ratios, increasing by only 1/3 from $[S]/[M] = 0.3$ to $[S]/[M] = 3.8$. Using the constants from Tobolsky and Offenbach(97) as in Section V-B-4, these G_R values become $(k_{t\ MM}/k_{11}^2 = 11{,}000$ moles/l.-sec.$)$:

[S]	[S]/[M]	G_R
2.47	0.3	0.32
6.81	1.1	0.34
11.5	2.6	0.34
13.2	3.8	0.42

The values are very close to the $G_R = 0.39$ calculated in Section V-B-4. The same constancy with composition change is noted in both studies, which together cover almost the complete range of reactant concentration ratios.

The effects of solvents were also studied. In particular, acetone completely inhibited the ionic reaction without appreciably affecting the rate of free radical copolymerization. Using 2% acetone, the authors obtained the following results for $[S]/[M] = 3$:

	WITHOUT ACETONE		WITH ACETONE	
T °C	n	S_p (mg)	n	S_p (mg)
30	2.09	122	1.89	130
20	1.85	115	1.65	114
0	1.62	111	1.36	110
-20	1.40	111	1.23	113
-78	1.45	121	1.07	120

The above results, calculated from Table 1 of their second paper,(55) show clearly that the yield of polymeric sulfur dioxide (S_p) is unchanged by the addition of acetone whereas the sulfur content of the polymer is sharply raised, especially at -78°. Further experiments at -78° demonstrated that, without acetone, the solubility in warm benzene went from 13% at $[S]/[M] = 2$ ($[S] = 10.3$) to 57% at $[S]/[M] = 11$ ($[S] = 19.0$) with the soluble fraction proving to be virtually pure styrene (0.6% sulfur). The insoluble fraction had the same composition as the polymers prepared with acetone; n was equal to about 1.1 and practically independent of composition. Their range of compositions at this temperature was limited by the freezing point curve for the system. According to Marvel and Glavis,(75) styrene and sulfur dioxide form a eutectic at

73 mole % SO_2 which freezes at -85°C, and the liquid region at -78° C extends from 68 to 87 mole % SO_2. Herz et al. found, however, that solutions above 60 mole % SO_2 were soluble at this temperature.

Figure V-11 summarizes their data for the acetone inhibited reaction. ln r_3p_3 is plotted vs. 1/T °K as in Figure V-10. For comparison, the data for the uninhibited reaction at $[S]/[M] = 3$ is also shown, as well as the curve from Figure V-10 representing the present data in this temperature range.

Note that there is very close correspondence between the 0° values of r_3p_3. These authors obtain $r_3p_3 = 5.4 \pm 1.1$ whereas the rate data from the present study give $r_3p_3 = 4.9 \pm 0.5$. These results demonstrate the usefulness of obtaining kinetic as well as composition data since while the composition data in this work was almost useless for determining r_3p_3, due to polystyrene formation. The rate of sulfur dioxide consumption was unaffected and proved a very accurate means of evaluating this propagation function.

In discussing the low temperature work of Barb,(7) the authors note that they were unable to obtain complete removal of polystyrene by extraction with benzene unless warm benzene was used and that cold chloroform, used by Barb to dissolve his polymers before precipitating them in benzene, will not dissolve some of the polymers prepared at -20°C. They therefore attribute Barb's finding of constant composition at -20° to incomplete removal of polystyrene and conjecture that his high n values at 0° C may be due to the use of cold benzene.

Dose rate dependence was examined by Herz et al.(54) at 30° C with one run each at 1,050 and 33,000 rad/min. The results show an

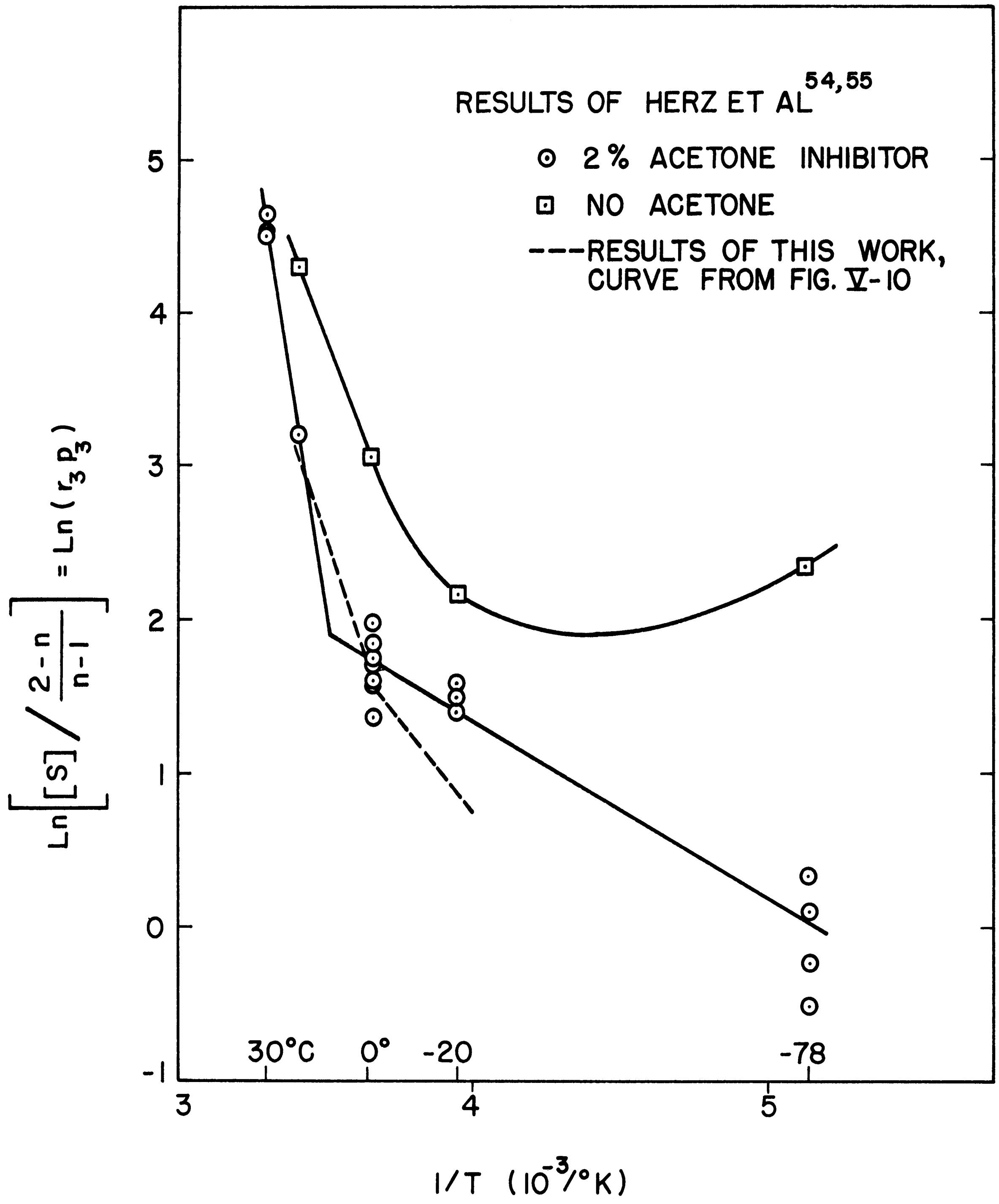

Figure V-11. Results of Herz, Hummel and Schneider.(54,55) Temperature Dependence of Polymer Composition from -78° to 30°C.

intensity exponent of 0.45 which, fortuitously, is identical to the value obtained in the present work from Figure V-14 at 0° C.

The high temperature graph, Figure V-12, is based on Equation (58), written in the form

$$(n-2)\ [S] = r_1 p_1\ (1 + p_2/[M])$$

Since only undiluted styrene was used, p_2 cannot be evaluated. Barb found p_2 to be equal to 0.9 at 20° and 3.1 at 60° which would make $(1 + p_2/[M])$ about 1.1 at 20° and 1.4 at 60°. Accordingly, some change in the slope of the Arrhenius plot is expected as p_2 becomes significant. This effect can be seen in Figure V-12, based on the equation

$$\ln\ \Big[(n-2)\ [S]\Big] = (E/R)\ 1/T + \ln A \tag{77}$$

where E is the activation energy for $r_1 p_1$ at low temperature (20°) and becomes the energy for $r_1 p_1 p_2$ at temperatures high enough so that $p_2/[M] \gg 1$. From the slopes of this plot, $E = 8$ kcal/mole for the lower part of the curve and changes to $E = 15$ kcal at the higher temperatures.

Barb's data for undiluted styrene is also shown, giving $E = 12$ kcal at the low end and $E = 17.5$ at higher temperatures. The two sets of values are not significantly different. Barb also presents data with diluted styrene ($[M] = 1.04$) and obtains the same effect at lower temperatures. This is to be expected since $p_2/[M]$ is now larger.

At the lower temperatures E is

$$E_{r_1 p_1} = E_{11} + E_{-12} - E_{12} - E_{21} = 8 \text{ kcal}\ , \tag{78}$$

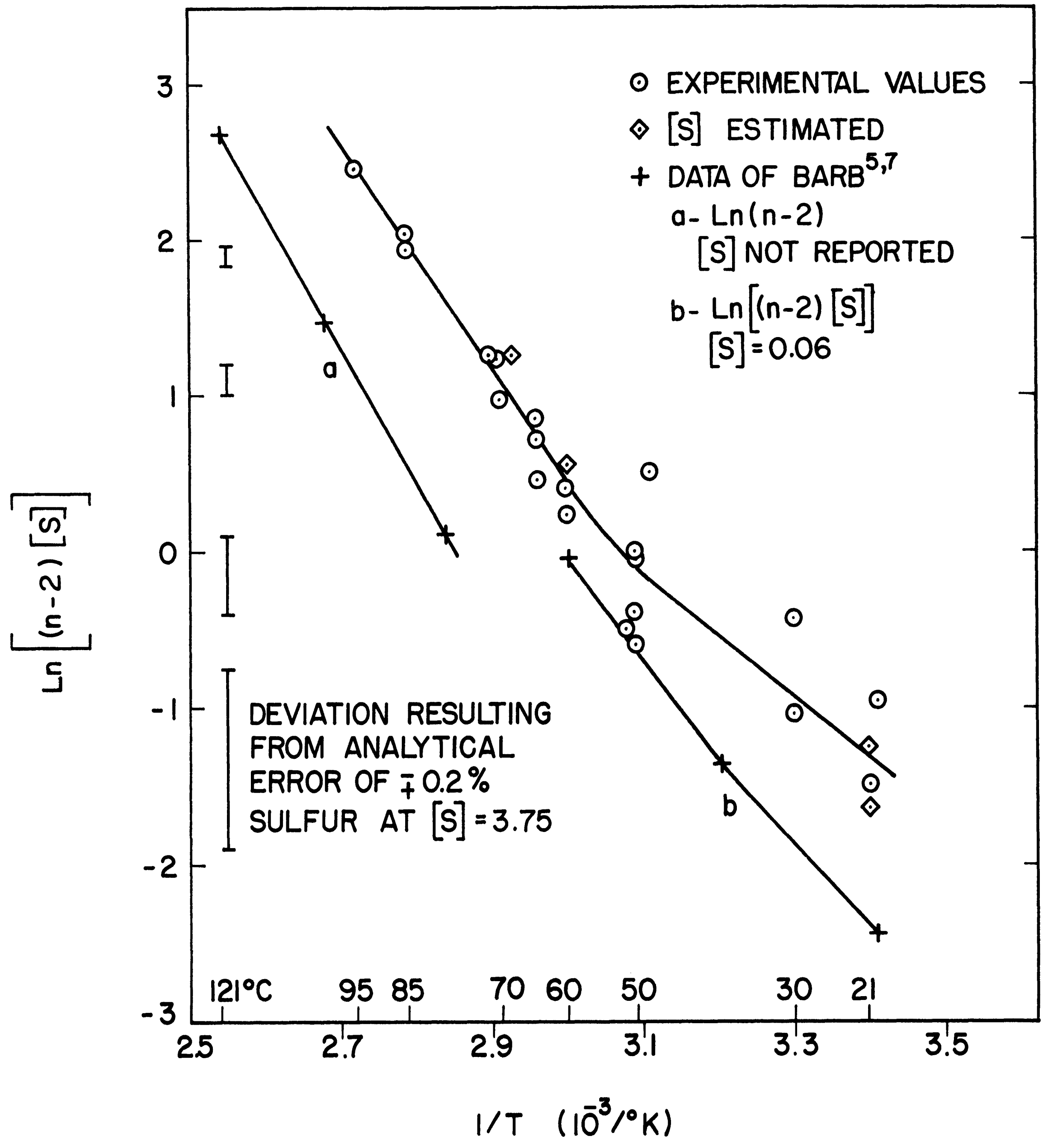

Figure V-12. Temperature Dependence of Polymer Composition - High Temperatures.

and at the highest temperatures it becomes

$$E_{r_1p_1p_2} = E_{-12} + E_{-21} - E_{12} - E_{21} = 15 \text{ kcal.} \qquad (79)$$

If [M] had varied appreciably at these temperatures it would have been necessary to plot ln $\left[(n-2)\ [S]\ [M]\right]$ to obtain Equation (79). Since from Matheson et al.(77) $E_{11} = 7.8$, subtracting (78) from (79) gives

$$E_{-21} = E_{11} + 7 = 15 \text{ kcal.}$$

Walling(115) estimates that E_{12} and E_{21} are each less than 5 kcal since reactions (5) and (6) to which they refer must be very rapid. Therefore, from (79) $5 < E_{-12} < 15$ with the upper value the limiting case for $E_{12} = E_{21} = 0$.

Figure V-12 also contains an additional effect. At each temperature above 21° the value of (n-2) [S] increases with increasing sulfur dioxide concentration, indicating that there is an additional dependence of [S] not accounted for by the postulated mechanism. Figure V-13 which compares the 60° (and 64°) composition data with that of Barb shows that this phenomenon is true for his data as well. The 64° data is corrected to 60° using the slope of the line in Figure V-11.

The data of Tokura and Matsuda(100) appear to contradict our results. They copolymerized styrene with sulfur dioxide at 40°, 50° and 60° using a free radical catalyst. The authors stated that the polymers in all cases had a composition of n=2 and interpreted this as resulting from the homopolymerization of a 2:1 complex of styrene and sulfur dioxide. The sulfur content of the polymers was not, however, determined by sulfur

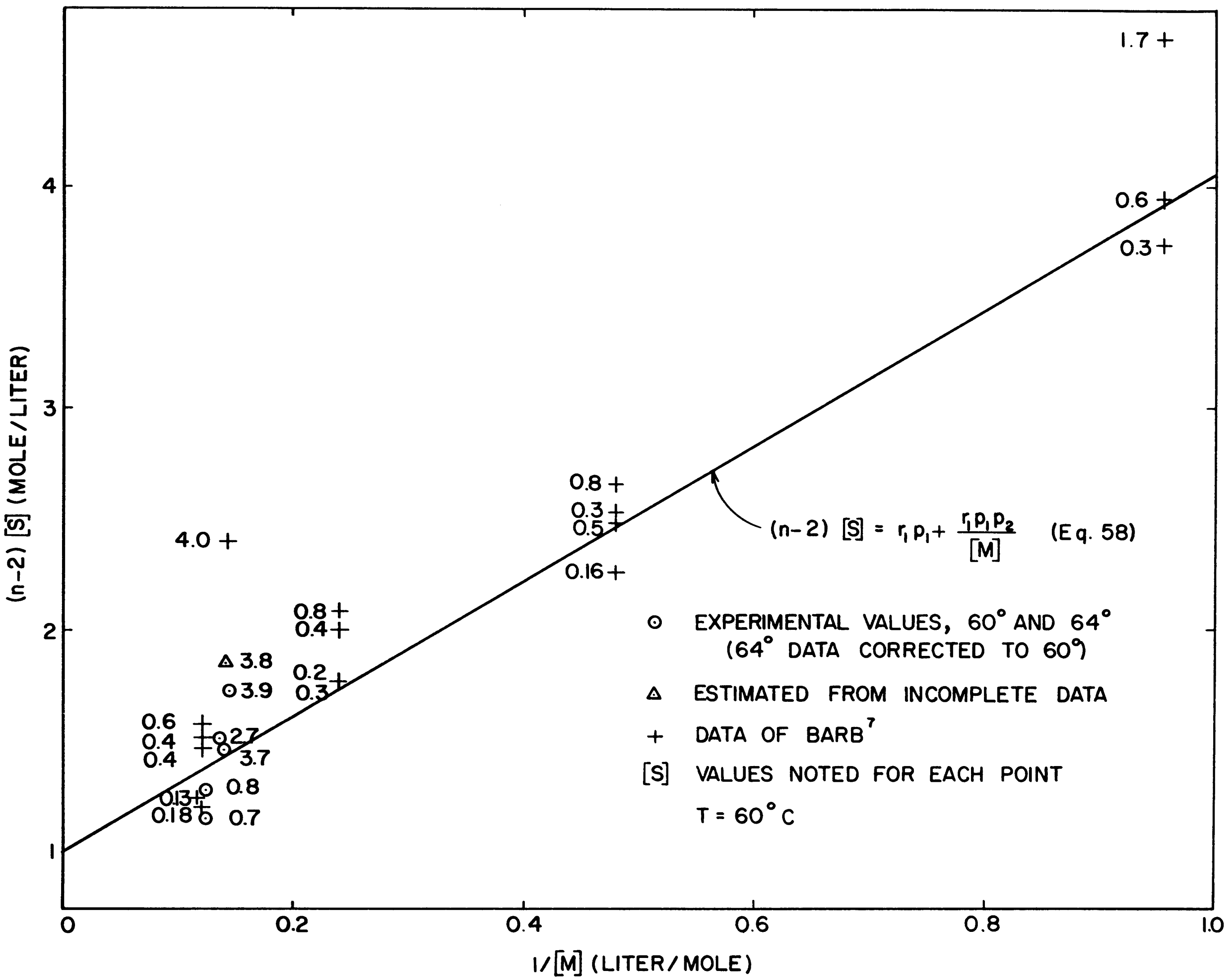

Figure V-13. Comparison of Composition Data at 60° and 64°C with data of Barb. Data at 64° Corrected to 60° Using Slope of Curve in Figure V-12. Sulfur Dioxide Concentration Noted for Each Point.

analysis but by difference from carbon and hydrogen analyses. In another paper, Tokura et al.(106) analyze for sulfur as well as for carbon and hydrogen in p-methylstyrene-sulfur dioxide copolymers. Comparing the sulfur content calculated from carbon and hydrogen analysis with that determined directly, it is seen that the indirect method results in an estimate which is high by an average of 1.3% SO_2 and by as much as 2.6% SO_2. If it is assumed that this same error exists in the styrene polysulfone analyses, the polymer compositions fall in the range where they can be predicted from the curve in Figure V-12 as shown below:

T °C	[S]	[S]/[M]	n Uncorrected	n Corrected	n Predicted
40	5.9	1.0	1.90	2.05	2.10
	8.5	1.7	1.83	1.97	2.07
	11.8	3.0	1.95	2.10	2.05
	11.8	3.0	1.82	1.95	2.05
50	5.9	1.0	1.94	2.08	2.15
	7.4	1.3	1.99	2.15	2.12
	8.5	1.7	1.95	2.10	2.10
	11.8	3.0	1.99	2.15	2.07
	11.8	3.0	1.79	1.92	2.07
	11.8	3.0	1.85	1.99	2.07
	11.8	3.0	1.78	1.90	2.07
	11.8	3.0	1.85	1.98	2.07
60	8.5	1.7	2.10	2.26	2.18
	8.5	1.7	2.09	2.25	2.18
	11.8	3.0	2.05	2.20	2.13
	11.8	3.0	1.99	2.15	2.13
	11.8	3.0	2.01	2.17	2.13

The values in the "n, corrected" column were obtained from values of sulfur dioxide content corrected by subtracting 1.3% SO_2 from the value obtained from C and H analyses. Even with this rough correction, the predicted values of n agree rather closely. At 40° and 50°, the scatter in the authors' data, mask the small predicted deviations from n=2. At 60°, however, the decrease in sulfur dioxide concentration becomes more pronounced (see Figure V-12) and is now clearly seen in their results. The choice of such high sulfur dioxide concentrations at these temperatures results in values of n so close to n=2 that considerable analytical accuracy is required to detect the deviations.

2. Rate Equations

At 50° and 60-64°, data was obtained over a wide enough range of sulfur dioxide concentrations to make use of the high temperature rate equations. At 50°, however, the data are scattered for unexplainable reasons. From the 60-64° data, shown separately in Figure V-7 a good fit to Equation (65a) is obtained with the data from both temperatures close enough to be combined, giving,

$$\frac{-\ [M]\ I^{1/2}}{d\ [S]\ dt} = 0.35 \times 10^{6} \left[1 + \frac{0.75}{[S]} \right] , \qquad (74)$$

where $k_{11}\ (k_i/k_{t\ MM})^{1/2} = (1/0.35)\ 10^{-6} = 3.1 \times 10^{-6}\ (\text{rad-min.})^{-1/2}$ and $r_1 p_1\ (1 + p_2/[M]) = 0.75$. The latter value is one half of the value obtained from the composition data (Figure V-11). Barb,(7) obtained a similar discrepancy and adequately reconciled it by assuming that at 60°, it was no longer possible to ignore $k_{t\ SM}$ and $k_{t\ SS}$ as is done in Equation (65a). Using Equation (66a), he found that if $\gamma = 2$, the rate data agreed with the composition equation (which does not involve termination rates).

If Equation (68) is rewritten in the same form as Equation (66a), we get

$$\frac{-[M]\ I^{1/2}}{d\ [S]/dt} = \left[\frac{k_{t\ MM}}{k_i}\right]^{1/2} \frac{\gamma}{k_{11}} \left[1 + \frac{r_1 p_1}{[S]} \ \frac{(1 + p_2/[M])}{\gamma}\right] \qquad (68a)$$

where $\gamma = 1 + \frac{k_{11}}{k_{21}} \frac{k_{t\ SM}}{k_{t\ MM}} (1 + \frac{p_2}{[M]})$.

From (74), $r_1 p_1 (1 + p_2/[M])\ \gamma = 0.75$ and from Figure V-11, $r_1 p_1 (1 + p_2/[M]) = 1.5$ at 60° C giving $\gamma = 2$, the same as calculated by Barb.

Returning to Figure V-9, the slopes of the sulfur dioxide reaction rate curve give overall activation energies for the reaction as $E_R = 0.6$ kcal/mole below 10° C and $E_R = 3.9$ kcal/mole between 10° and 50° C. Above 50° the effects of depropagation are apparent and E_R starts to decrease as k_{-21} becomes more significant as indicated by an increasing value of p_2. This does not affect the rate of styrene consumption as shown by curve 1. In fact, a comparison of Equation (70) and (70a) shows that at a temperature high enough for $r_1 p_1$ and p_2 in Equation (70) to be large enough to make the second term in the brackets negligible, the equation reduces to Equation (70a), the equation for pure styrene.

3. Styrene Polymerization

Curve 3 in Figure V-9 shows the data for pure styrene polymerization with the slope of the upper portion fitted by the values $E_{11} = 7.8$ and $E_{t\ MM} = 2.4$ from Matheson et al.,(77) where $E_R = E_{11} - 1/2\ E_{t\ MM} = 6.6$ kcal/mole. While this slope fits the upper points well, the points at 0° and -21° are much too high, indicating the presence of a simultaneous ionic polymerization at the low temperatures. As noted in Section B, Chen(26) also obtained this effect at lower temperatures by irradiating pure styrene at dose rates of 20 and 56 k rad/min. With these much higher dose rates, the ionic effect should be noticeable at higher temperatures, but Chen's much more elaborate purification procedure(25) may account for the discrepancy.

4. Thermal Initiation

Several runs were made without radiation to determine if the rate of thermal initiation was negligible compared to that due to radiation. The results are as follows:

Run No.	T °C	Time Min.	Yield		Thermal rate/ Radiation Rate
			Wt. %	Wt. %/hr.	
122	0	200	0.035	0.008	0.02
132	0	200	0.022		
133	0	200	0.020		
216	0	1380	0.040	0.002	0.005
200	60	73	0.074	0.06	0.06
*	68	-	-	0.22	0.17

* Initial rate for pure styrene from Boundy and Boyer.(11)

From the results at 0° C it is seen that most of the thermal reaction took place in a relatively short time. Comparing Run No. 216 with the three 200 minute runs, more polymer was formed in the first 200 minutes than in the succeeding 20 hours. This probably explains why the 15 minute runs gave a higher overall rate than did the 30-200 minute runs. The result at 60° suggests that at still higher temperatures, thermal initiation would have to be considered. This is to be expected since, whereas $E_i = 0$ for radiation initiation, $E_i \gg 0$ for thermal initiation (about 29 kcal/mole for styrene),(44) thereby increasing E_R, the overall activation energy for the reaction. This effect is not noticeable in Figure V-9.

Since no dark runs were made with pure styrene, a value from the literature was used, which may not be valid for these conditions since a 17% increase should have resulted in a noticeably steeper slope in curve 3 in Figure V-9.

D. Variation in Radiation Intensity

Figure V-14 shows the variation in reaction rates with radiation intensity for both sulfur dioxide and styrene. The reactant composition is normalized to $[S] = 3.75$ moles/liter using the slopes of the curves in Figure V-3.

For sulfur dioxide the reaction rate is seen to be proportional to $I^{0.45}$ where for styrene consumption, it is proportional to $I^{0.48}$. Both of these values are close to the predicted $I^{1/2}$ dependence.

The effect of the ionic side reaction should show up as an increase in slope of the $-d\,[M]/dt$ curve at the higher dose rates since this reaction has been found to have a rate proportional to the first power of the radiation intensity. This effect can be seen if a line parallel to the $-d\,[S]/dt$ curve is drawn through the low intensity points. This curve is shown as a dashed line in Figure V-14 and is seen to fit the low solubility point at 1400 rad/min. as well as the two lower dose rate points. The high solubility 1400 rad/min. point as well as the 6040 rad/min. points lie above this line. Note that the highest 6040 rad/min. value is from Run No. 217 which had the highest benzene solubility at 0° C.

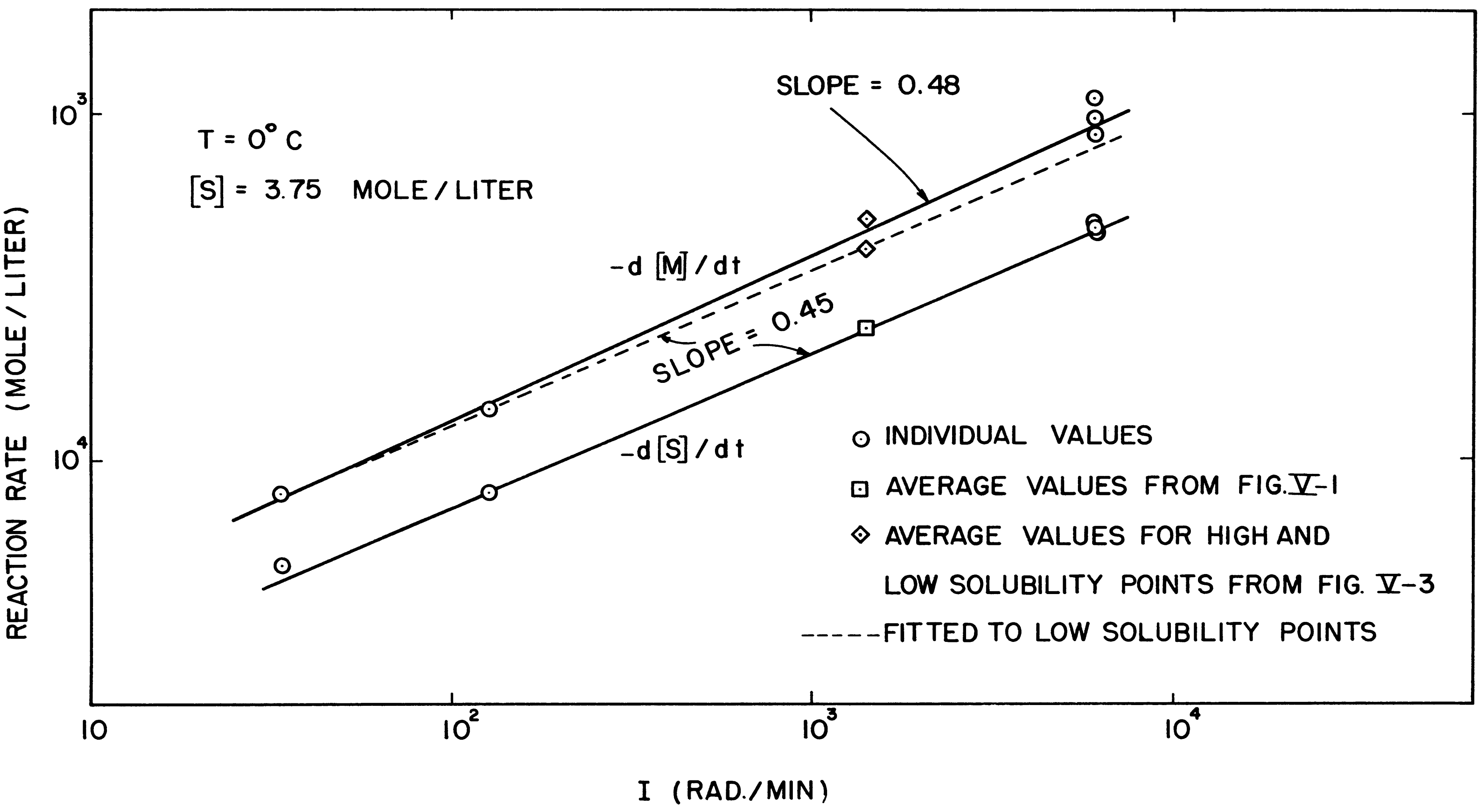

Figure V-14. Dose Rate Dependence of Reaction Rates. All Values Adjusted to [S] = 3.75.

VI SUMMARY AND CONCLUSIONS

The copolymerization of styrene and sulfur dioxide, initiated by gamma radiation was studied over the temperature range of -21° to +95°C. The reaction was the most thoroughly investigated at 0°C with the initial SO_2/styrene molar ratio varying from 0.03 to 1.1. The radiation intensity dependence was determined over the range from 33.4 to 6040 rad/min. The rate was found to be proportional to $I^{0.45}$.

At 0°C, the reaction rate data fit the rate equation derived on the basis of the free radical mechanism proposed by Barb(5,6,7) and Walling(115), giving

$$\frac{-d\,[S]/dt}{I^{1/2}\,[M]} = 4.8 \times 10^{-7} \left[1 + \frac{[S]}{4.9}\right] \text{rad}^{-1/2}\ \text{min}^{-1/2} \,.$$

The G value for radical production was calculated as $G_R = 0.39$ radicals/100 ev.

At 60° and 64°C the rate data fit the equation

$$\frac{-I^{1/2}\,[M]}{d\,[S]/dt} = 0.35 \times 10^{6} \left[1 + \frac{0.75}{[S]}\right] \text{rad}^{1/2}\ \text{min}^{1/2}$$

Evidence is given for a competing ionic mechanism at 0°C, yielding polystyrene and reducing the apparent sulfur dioxide content of the polymers. This competing reaction did not noticeably affect the rate of reaction of sulfur dioxide.

The activation energies for the propagation functions were estimated from the composition data. At 0°C and below

$$E_{r_3p_3} = E_{11} + E_{-32} - E_{32} - E_{21} = 4.9 \text{ kcal/mole},$$

below 50°C,

$$E_{r_1p_1} = E_{11} + E_{-12} - E_{12} - E_{21} = 8 \text{ kcal/mole}$$

and above 50°C

$$E_{r_1p_1p_2} = E_{-12} + E_{-21} - E_{12} - E_{21} = 15 \text{ kcal/mole},$$

giving (with $E_{11} = 7.8$ from the literature)

$$E_{-21} = 15 \text{ kcal/mole}$$

Comparisons are made with the data of Barb(5,6,7), Tokura, *et al.*(100) and Herz, Hummel and Schneider.(54,55) The 0°C rate data was found to agree closely with the composition data of Herz, *et al.*(55) at the same temperature giving $r_3p_3 = 4.9 \pm 0.5$ compound to their $r_3p_3 = 5.4 \pm 1.1$ for the mean and standard deviation of the data. Their work was the only other study involving radiation initiation of this reaction.

This study and the work of Herz, Hummel and Schneider together give a reasonably good picture of the radiation copolymerization of styrene and sulfur dioxide over almost the entire range of reactant ratios.

There are, however, a number of gaps which should be filled:

1. The temperature range above 65° is almost unexplored. No work has been done above 95°C.

2. No work has been done at high sulfur dioxide concentrations above 30°C.

3. The extent of ionic reaction at $0^{\circ}C$ did not show any consistency. The reason is unknown but it is likely that uncontrolled variations in purity (perhaps in water concentration) would have some effect. A further study of this aspect will be aided by the discovery by Herz, et al.(55) that low concentrations of acetone will completely inhibit the ionic initiation without changing the free radical copolymerization rate.

APPENDIX A

TABLE I

EXPERIMENTAL CONDITIONS AND RESULTS

Reaction Conditions						Reactant Charge					Product		
Run No.	Date of Run	Temperature °C	Time min.	Dose Rate rad/min	Total Dose kilorads	Styrene + SO$_2$ grams	SO$_2$ millimoles	Styrene millimoles	[S]/[M] Molar Ratio	Vol. ml.	Polymer grams	Sulfur Analysis % Sulfur	Solubility in Benzene %
		122-131 Distilled 6-21-61											
122	6-24-61	0	200	0	0	19.72	48.6	160	.30	19.9	.0070	--	--
124	6-24-61	0	101	1460	147	19.63	43.0	162	.26	20.0	.1290	11.54	14
125	6-24-61	0	101	1440	145	21.15	69.4	161	.43	20.9	.1335	11.54	17
126	6-24-61	0	101	1420	143	24.74	121	163	.74	23.6	.1680	11.55	18
127	6-24-61	0	101	1420	143	25.37	133	162	.82	23.9	.1785	11.73	19
128	6-24-61	0	200	1460	292	20.02	42.7	166	.26	20.4	.2825	11.63	12
129	6-24-61	0	200	1440	288	21.52	78.7	158	.50	21.1	.3005	11.56	19
130	6-24-61	0	200	1440	288	23.48	100	164	.61	22.6	.3225	11.49	17
131	6-24-61	0	200	1420	284	25.33	130	163	.80	23.9	.3415	11.34	21
		132-143 Distilled 7-13-61											
132	7-20-61	0	200	0	0	22.94	84.8	168	.50	22.5	.0050	--	--
133	7-20-61	0	200	0	0	25.19	123	166	.74	24.0	.0050	--	--
134	7-20-61	0	60	1450	87	19.67	33.7	168	.20	20.3	.0765	10.58	16
135	7-20-61	0	60	1430	86	23.63	95.0	168	.56	23.2	.0915	11.19	14
136	7-20-61	0	60	1410	85	26.54	141	168	.84	24.8	.0925	13.00	09
137	7-20-61	0	30	1440	43.2	20.82	46.2	171	.27	21.0	.0405	10.37	--
138	7-20-61	0	30	1430	42.9	23.79	88.8	174	.51	23.3	.0480	10.90	--
139	7-20-61	0	30	1410	42.3	26.62	139	170	.82	25.1	.0515	12.01	--
140	7-20-61	0	15	1450	21.8	20.31	38.1	171	.22	20.7	.0225	--	--
141	7-20-61	0	15	1430	21.4	23.75	96.5	169	.57	23.1	.0250	10.70	--
142	7-20-61	0	15	1410	21.2	26.93	142	171	.83	25.4	.0300	11.11	--
143	7-20-61	0	15	1440	21.6	20.64	42.6	172	.23	20.8	.0225	--	--
		144-153 Distilled 8-2-61											
144	8-7-61	0	15	1440	21.6	18.92	10.8	175	.06	20.1	.0145	--	--
145	8-7-61	0	15	1440	21.6	19.49	27.3	170	.16	20.1	.0160	--	--
146	8-7-61	0	15	1440	21.6	18.88	17.5	170	.10	19.9	.0145	--	--
147	8-7-61	0	15	1320	19.8	28.71	168	172	.98	26.6	.0255	--	--
148	8-7-61	0	100	1440	144	18.46	11.1	170	.07	19.6	.0950	11.63	02
149	8-7-61	0	100	1430	143	19.18	21.8	171	.13	20.2	.0995	12.12	02
150	8-7-61	0	100	1430	143	19.64	23.6	174	.14	20.8	.1040	12.26	03
151	8-7-61	0	100	1320	132	29.90	189	171	1.10	27.4	.1685	14.06	03
152	8-7-61	0	30	1440	43.2	18.57	11.1	171	.07	19.8	.0280*	--	--
153	8-7-61	0	30	1440	43.2	19.06	20.4	170	.12	19.9	.0290*	--	--
		154-177 Distilled 9-27-61											
154	10-11-61	0	200	1370	274	19.11	15.9	174	.09	20.1	.2000	11.16	07
155	10-11-61	0	60	1370	82.2	18.60	11.4	171	.07	19.8	.0575	--	--
156	10-11-61	0	15	1370	20.6	18.80	8.9	175	.05	20.0	.0165	--	--
157	10-11-61	0	200	1370	274	18.35	7.8	171	.05	19.5	.2030	10.25	15
158	10-11-61	0	60	1370	82.2	18.41	8.0	172	.05	19.6	.0590	--	--
159	10-11-61	0	15	1370	20.6	19.21	18.7	173	.11	20.2	.0175	--	--
160	10-11-61	0	200	1370	274	17.90	0	172	0	19.4	.0920	0	--
161	10-11-61	0	60	1370	82.2	17.87	0	172	0	19.3	.0290	0	--
162	10-11-61	0	60	1300	78.0	29.13	172	174	.99	27.0	.1120	11.39	20
163	10-11-61	0	15	1300	19.5	29.07	177	170	1.04	26.9	.0335	--	--
164	10-17-61	0	100	1370	137	18.49	8.1	173	.05	19.7	.0845	10.78	08
165	10-17-61	0	100	1370	137	19.35	22.6	172	.13	20.2	.0940	11.97	05
166	10-17-61	0	100	1360	136	20.32	34.5	174	.20	20.9	.1025	12.30	05
167	10-17-61	0	100	1360	136	20.86	44.6	173	.26	21.1	.1245	11.15	15
168	10-17-61	0	100	1360	136	21.01	47.4	173	.27	21.2	.1255	11.46	12
169	10-17-61	0	100	1350	135	21.79	60.2	172	.35	21.8	.1315	11.49	12
170	10-24-61	21	60	1340	80.4	(23.4)	(87)	171	(.51)	(23.2)	.1195	11.62	--
171	10-24-61	21	60	1350	81.0	(20.5)	(40)	173	(.23)	(21.4)	.1090	11.12	--
172	10-24-61	21	60	1350	81.0	20.46	40.7	171	.24	21.3	.1040	11.07	--
173	10-24-61	21	60	1340	80.4	23.74	89.1	173	.51	23.5	.1195	11.87	05
174	10-24-61	10	60	1350	81.0	(20.4)	(40)	172	(.23)	(21.0)	.0825	10.98	--
175	10-24-61	10	60	1340	80.4	(23.5)	(87)	172	(.51)	(23.0)	.0915	11.82	10
176	10-24-61	30	60	1350	81.0	20.36	36.5	173	.21	21.4	.1370	10.70	07
177	10-24-61	30	60	1340	80.4	23.56	84.1	174	.48	23.8	.1548	11.36	05

TABLE I (CONT'D)

Reaction Conditions						Reactant Charge					Product		
Run No.	Date of Run	Temperature °C	Time min.	Dose Rate Rad/Min	Total Dose kilorads	Styrene + SO_2 grams	SO_2 millimoles	Styrene millimoles	[S]/[M] Molar Ratio	Vol. ml.	Polymer grams	Sulfur Analysis % Sulfur	Solubility in Benzene %
	178-200 Distilled 11-6-61												
178	11-8-61	20	60	1330	79.8	23.88	91.5	173	.53	23.6	.1270	11.30	--
181	11-13-61	10	30	1330	39.9	22.85	75.1	173	.44	22.6	.0425	12.36	--
182	11-13-61	10	60	1330	79.8	23.14	80.2	173	.46	22.9	.0860	12.44	--
183	11-13-61	10	120	1330	160	23.19	78.5	174	.45	23.0	.1740	12.51	04
184	11-18-61	0	495	1350	668	18.62	5.8	175	.03	20.0	.4750	10.82	09,11
185	11-18-61	0	495	1330	658	23.47	84.0	174	.48	23.0	.7820	13.05	07,06
186	11-22-61	70	30	1320	39.6	(23.5)	(81)	176	(.46)	(24.7)	.1750	--	--
187	11-22-61	70	60	1330	79.8	22.47	68.5	174	.40	23.6	.3375	--	--
188	11-22-61	70	121	1320	160	24.49	100.4	173	.58	25.5	.6662	8.81	96
189	11-22-61	70	240	1320	317	23.56	87.9	172	.51	24.3	1.3255	9.18	98
190	12-1-61	50	10	1320	13.2	23.41	85.9	172	.50	23.9	.0524	10.71	--
191	12-1-61	50	30	1320	39.6	24.09	97.4	171	.57	24.3	.1278	10.80	--
192	12-1-61	50	30	1340	40.2	19.50	23.9	173	.14	21.2	.1090	9.60	28
193	12-6-61	85	10	1320	13.2	24.12	94.6	173	.55	25.4	.0810	6.57	--
194	12-5-61	-10	30	1320	39.6	23.54	86.2	173	.50	22.9	.0355	12.79	--
195	12-5-61	-10	120	1320	158	23.45	84.0	173	.48	22.8	.1525	13.13	11
196	12-6-61	85	40	1320	52.8	24.12	94.4	173	.54	25.4	.2815	6.81	99
197	12-22-61	60	60	1310	78.6	(24.0)	(94)	173	(.55)	(24.5)	.2883	9.95	11
198	12-10-61	95	30	1320	39.6	24.02	94.9	172	.55	25.6	.2367	5.37	99
200	12-22-61	60	73	0	0	(24.0)	(95)	172	(.55)	(24.5)	.0178	--	--
	201-225 Distilled 1-24-62												
201	2-2-62	-21	180	1310	236	19.50	23.0	173	.13	20.1	.1150	12.76	07
202	2-2-62	-21	180	1290	232	24.67	104.7	172	.61	23.5	.2132	14.57	06
203	2-6-62	-21	252	1320	333	17.39	0	167	0	18.5	.0699	0.	--
204	2-8-62	64.3	60	1320	79.2	17.68	0	169	0	20.4	.2395	0.	--
205	2-8-62	64.3	60	1310	78.6	18.85	15.0	172	.09	21.2	.2610	6.40	98
206	2-8-62	64.3	60	1300	78.0	22.05	63.6	173	.37	23.5	.2990	9.16	75,90
											Sol.	8.68**	
207	2-8-62	64.3	60	1290	77.4	23.66	94.2	169	.56	24.4	.2971	9.58	20
208	2-17-62	48.5	60	1310	78.6	17.94	0	172	0	20.4	.1313	0.	--
209	2-20-62	68.4	60	1310	78.6	17.55	0	169	0	20.3	.2330	0.	99
210	2-17-62	48.5	60	1250	75.0	27.30	148.1	171	.86	26.8	.2414	10.53	--
211	2-20-62	68.4	60	1250	75.0	27.90	(157)	(171)	(.92)	27.6	.3199	9.52	27
212	3-6-62	59.9	90	1290	116	19.15	17.3	173	.10	21.3	.3630	7.39	96
213	3-6-62	59.9	90	1270	114	23.77	89.7	173	.52	24.0	.4144	10.16	06
215	3-15-62	0	900	33.4	30.1	23.90	94.9	171	.55	23.2	.2442	13.72	03
216	3-15-62	0	1380	0	0	23.71	92.6	171	.54	23.0	.0096	--	--
217	3-21-62	0	30	6040	181	24.06	96.3	172	.56	23.4	.1055	10.58	27
218	3-21-62	0	90	6040	544	23.74	87.8	174	.50	23.3	.2736*	11.23	19,21
219	4-26-62	0	300	128	38.4	24.09	95.4	173	.55	23.4	.1409	12.92	05
220	4-27-62	0	61	6040	368	22.83	79.0	170	.46	22.4	.1720	12.23	14
222	4-29-62	0	1660	1250	2075	(23.4)	(86)	172	(.53)	(22.9)	4.06	13.64	07
223	5-20-62	51.2	90	1260	113	19.97	33.4	171	.20	21.5	.3130	10.15	07
224	5-20-62	50.5	94	1260	118	18.99	21.3	169	.13	20.9	.2439	9.66	17
225	5-20-62	71.5	55	1200	66.0	28.19	160.0	172	.93	27.9	.3118	9.53	47,41,38
											Sol.	8.80**	--
											Insol.	9.97**	--

* Small loss of polymer.

** Analyses of the soluble and insoluble fractions from the benzene solubility test.

() Estimated from incomplete reactant weight data.

TABLE II

DOSIMETRY RESULTS

	Center Well			PRF Source			
Position No. see note	Depth of Soln. (inches)	Time (min.)	Optical Density	T °C	Dose krad	Dose Rate rad/min.	Date
Solutions Mixed							
Dewar A							
14	3	16	0.753	24	21.0	1313	6-5-62
15	3 1/2	25 1/4	0.170	24	32.6	1293	6-5-62
5	3 1/2	25 1/4	1.180	24	32.9	1304	6-5-62
3	4	16	0.740	24	20.6	1290	6-5-62
12	4	16	0.735	24	20.5	1282	6-5-62
1	4	16	0.738	24	20.6	1287	6-5-62
3	4	25 1/4	1.165	24	32.5	1287	6-5-62
1	4	25 1/4	1.165	24	32.5	1287	6-5-62
13	4 1/8	25 1/4	1.150	24	32.1	1270	6-5-62
16	4 1/2	25 1/4	1.130	24	31.5	1249	6-5-62
Dewar B							
6	3 1/2	20	0.898	24	25.0	1253	6-5-62
15	3 1/2	20	0.910	24	25.4	1269	6-5-62
4	4	20	0.892	24	24.9	1244	6-5-62
3	4	20	0.898	24	25.0	1253	6-5-62
16	4	20	0.894	24	24.9	1247	6-5-62
1	4 1/2	20	0.870	24	24.3	1214	6-5-62

TABLE II (CONT'D)

Position No. see note	Depth of Soln. (inches)	Time (min.)	Optical Density	T °C	Dose krad	Dose Rate rad/min.	Date
			Solutions Not Mixed				
			Dewar A				
4	3	30	1.415	23	39.7	1325	6-3-62
12	3	23	1.075	23	30.2	1313	6-3-62
6	3 1/2	30	1.400	23	39.3	1311	6-3-62
14	3 1/2	23	1.100	23	30.9	1344	6-3-62
1	4	30	1.345	23	37.8	1260	6-3-62
3	4	30	1.360	23	38.2	1274	6-3-62
16	4	23	1.080	23	30.3	1319	6-3-62
1	4	23	1.070	23	30.1	1307	6-3-62
2	4	23	1.060	23	29.8	1295	6-3-62
15	4 1/2	30	1.325	23	37.2	1241	6-3-62
4	4 1/2	23	1.030	23	28.9	1258	6-3-62
6	5	23	1.035	23	29.1	1265	6-3-62
			Dewar B				
4	3	30	1.370	23	38.5	1283	6-3-62
6	3 1/2	30	1.330	23	37.4	1246	6-3-62
1	4	30	1.320	23	37.1	1236	6-3-62
3	4 1/2	30	1.300	23	36.5	1218	6-3-62
15	5	30	1.260	23	35.4	1180	6-3-62
South	3	11	0.518	24	14.45	1314	4-15-62
South	3 1/2	11	0.500	24	13.95	1268	4-15-62
South	4	11	0.492	23	13.83	1257	4-15-62
South	4	11	0.488	23	13.71	1238	4-15-62
South	4 1/2	11	0.472	24	13.17	1206	4-15-62
South	3 1/2	8 1/6	0.376	24	10.49	1284	4-16-62
South	4	8 1/6	0.370	24	10.32	1260	4-16-62
South	4	8 1/6	0.370	24	10.32	1264	4-16-62
South	4	12 1/6	0.535	24	14.93	1227	4-16-62
South	4	12 1/6	0.548	24	15.29	1257	4-16-62

Note: For the dosimetry done on June 3 and 5 positions were noted exactly. The circumference was divided into 16 positions with 1 = South, 5 = West, 9 = North and 13 = East. The empty Co-60 rod hole is in the 6 1/2 position.

TABLE II (CONT'D)

North Side of Source PRF Source

Distance from Source* (cm.)	Time min.	Optical Density	T °C	Dose krad	Dose Rate rad/min.	Date	Dose Rate Corrected to 4-1-62
70.5	360	0.433	27	11.82	32.8	4-5-62	32.9
10	52	0.806	25	22.33	429	4-9-62	431
20	52	0.384	26	10.56	203.1	4-9-62	203.8
30	52	0.225	26	6.19	119.0	4-9-62	119.4
40	52	0.141	25	3.91	75.2	4-9-62	75.5
38	240	0.738	24	20.59	85.8	4-15-62	86.3
54	240	0.432	24	12.05	50.2	4-15-62	50.5
65.7	240	0.328	24	9.15	38.1	4-15-62	38.3
76	240	0.260	24	7.25	30.2	4-15-62	30.4
100	240	0.162	24	4.52	18.8	4-15-62	18.2

* Distance measured horizontally from outside of source basket.

Center Well PML Source

400 m.l. Dewar Raised 2 Inches Above Bottom of Center Well.

Depth of Soln. inches	Time min.	Optical Density	T °C	Dose krad	Dose Rate rad/min.	Date	Dose Rate Corrected to 4-1-62
4	4	0.888	25	24.42	6105	4-5-62	6117
4	4	0.875	24.5	24.32	6080	4-16-62	6114
4	4	0.860	24.5	23.91	5978	4-16-62	6011
4 1/2	4	0.865	24.5	24.05	6012	4-16-62	6045
						AVERAGE	6072

TABLE IV

CALCULATED RESULTS

LOW TEMPERATURES

Run No.	[S] mole/l.	[M] mole/l.	n	$\frac{1}{n-1}$	[Sp] see note-1	$\frac{-d[S]/dt}{[M]\ I^{1/2}}$ (rad-min.)$^{-1/2}$	$\frac{-d[M]/dt}{[M]\ I^{1/2}}$ (rad-min.)$^{-1/2}$	$\frac{1}{n_o-1}$ see note-2
	0°C					x 10^{-6}	x 10^{-6}	
122	2.44	8.03	---	---	---	---	---	---
124	2.15	8.09	2.05	0.95	0.0232	0.74	1.52	1.47
125	3.31	7.69	2.05	0.95	0.0229	0.78	1.60	1.67
126	5.14	6.92	2.05	0.95	0.0256	0.97	1.99	1.75
127	5.56	6.77	2.00	1.00	0.0272	1.05	2.10	2.00
128[c]	2.07	8.07	2.03	0.95	0.0500	0.81	1.64	1.35
129	3.73	7.49	2.05	0.95	0.0516	0.91	1.87	1.85
130	4.43	7.26	2.07	0.95	0.0513	0.93	1.93	1.61
131	5.44	6.82	2.10	0.91	0.0504	0.98	2.06	1.89
132	3.77	7.47	---	---	---	---	---	---
133	5.13	6.92	---	---	---	---	---	---
134	1.66	8.28	2.30	0.77	0.0125	0.66	1.52	1.20
135	4.10	7.25	2.13	0.87	0.0138	0.84	1.79	1.33
136	5.68	6.77	1.75	1.33	0.0151	0.99	1.73	1.85
137	2.20	8.13	2.35	0.74	0.0062	0.67	1.57	---
138	3.81	7.46	2.21	0.83	0.0069	0.82	1.80	---
139	5.54	6.77	1.95	1.05	0.0076	0.99	1.93	---
140	1.84	8.25	2.60	0.62	0.0032	0.68	1.77	---
141	4.18	7.33	2.26	0.80	0.0036	0.87	1.97	---
142	5.59	6.73	2.15	0.87	0.0041	1.08	2.32	---
143	2.04	8.25	---	---	---	---	---	---
144	0.54	8.69	---	---	---	---	---	---
145	1.36	8.46	---	---	---	---	---	---
146	0.88	8.56	---	---	---	---	---	---
147	6.32	6.47	---	---	---	---	---	---
148[c]	0.56	8.64	2.03	0.95	0.0175	0.53	1.08	1.03
149[c]	1.07	8.45	1.92	1.05	0.0186	0.58	1.11	1.15
150[c]	1.13	8.35	1.90	1.11	0.0192	0.61	1.16	1.20
151	6.90	6.24	1.58	1.72	0.0270	1.19	1.88	1.96
152	0.56	8.64	---	---	---	---	---	---
153	1.03	8.54	---	---	---	---	---	---
154[c]	0.77	8.60	2.15	0.87	0.0348	0.54	1.16	1.05
155	0.58	8.64	---	---	---	---	---	---
156	0.44	8.75	---	---	---	---	---	---

TABLE IV (CONT'D)

Run No.	[S] mole/l.	[M] mole/l.	n	$\frac{1}{n-1}$	[Sp] see note-1	$\frac{-d[S]/dt}{[M]\ I^{1/2}}$ (rad-min.)$^{-1/2}$	$\frac{-d[M]/dt}{[M]\ I^{1/2}}$ (rad-min.)$^{-1/2}$	$\frac{1}{n_o-1}$ see note-2
	0°C					x 10^{-6}	x 10^{-6}	
157^c	0.38	8.73	2.39	0.72	0.0331	0.51	1.22	1.06
158	0.41	8.78	---	---	---	---	---	---
159	0.93	8.56	---	---	---	---	---	---
160	0	8.87	inf.	0	0	---	0.69	0
161	0	8.91	inf.	0	0	---	0.73	0
162	6.37	6.44	2.09	0.91	0.0147	1.05	2.19	1.82
163	6.58	6.32	---	---	---	---	---	---
164	0.40	8.76	2.25	0.80	0.0140	.43	0.97	0.98
165	1.12	8.51	1.96	1.05	0.0174	.55	1.08	1.20
166	1.65	8.33	1.88	1.11	0.0188	.61	1.15	1.30
167	2.11	8.20	2.15	0.87	0.0206	.68	1.46	1.35
168	2.24	8.16	2.07	0.95	0.0213	.71	1.47	1.33
169	2.76	7.89	2.06	0.95	0.0216	.75	1.55	1.35
184^c	0.25	8.66	2.23	0.80	0.0800	0.51	1.14	1.03
185^c	3.58	7.45	1.75	0.33	0.139	1.03	1.80	1.72
215	4.09	7.37	1.63	1.54	0.0450	1.17	1.90	1.75
216	4.03	7.43	---	---	---	---	---	---
217	4.12	7.35	2.29	0.77	0.0150	0.87	2.00	1.96
218	3.77	7.47	2.13	0.87	0.0411	0.79	1.68	1.72
219	4.08	7.39	1.77	1.33	0.0243	0.97	1.71	1.54
220	3.53	7.59	1.90	1.11	0.0293	0.81	1.54	1.82
222^c	3.00	6.90	1.64	1.54	(0.752)	1.85	3.04	2.08
	+ 10°C.	(see also Table V)						
174	(1.90)	(8.2)	2.19	0.84	(0.0135)	(0.75)	(1.64)	---
175	(3.78)	(7.5)	1.98	1.01	(0.0147)	(0.89)	(1.76)	1.37
181	3.32	7.65	1.88	1.14	0.0073	0.87	1.63	---
182	3.50	7.55	1.86	1.16	0.0145	0.88	1.63	---
183	3.41	7.57	1.85	1.18	0.0295	0.89	1.65	1.33
	- 10°C.							
194	3.76	7.58	1.79	1.26	0.0062	0.75	1.34	---
195	3.68	7.61	1.73	1.37	0.0274	0.83	1.43	2.12
	- 21°C.							
201^c	1.13	8.59	1.80	1.25	0.0228	0.41	0.73	1.59
202	4.46	7.32	1.50	1.20	0.0414	0.87	1.31	2.70
203	0	9.03	inf.	0	0	0	0.44	0

note-1 $[Sp] = \frac{\text{moles } SO_2 \text{ in polymer}}{\text{liter of reactant solution}}$

note-2 n_o = n calculated on the basis of the weight of the insoluble polymer fraction.

TABLE V

CALCULATED RESULTS

HIGH TEMPERATURES

Run No.	T °C	[S] mole/l.	[M] mole/l.	n	$[S_p]$ see note-1	$\frac{-d[S]/dt}{[M]\ I^{1/2}}$ $(\text{rad-min.})^{-1/2}$ $\times 10^{-6}$	$\frac{-[M]\ I^{1/2}}{d[S]/dt}$ $(\text{rad-min.})^{+1/2}$ $\times 10^{-6}$	$\frac{-d[M]/dt}{[M]\ I^{1/2}}$ $(\text{rad-min.})^{-1/2}$ $\times 10^{-6}$
170	21	(3.75)	(7.37)	2.03	(0.0186)	(1.15)	(0.87)	(2.34)
171	21	(1.87)	(8.08)	2.15	(0.0177)	(0.99)	(1.01)	(2.14)
172	21	1.91	8.03	2.17	0.0169	0.96	1.04	2.06
173	21	3.79	7.36	1.98	0.0189	1.17	0.86	2.32
174	10	(1.90)	(8.2)	2.19	(0.0135)	(.75)	(1.33)	(1.64)
175	10	(3.78)	(7.5)	1.98	(0.0147)	(.89)	(1.12)	(1.76)
176	30	1.71	8.08	2.27	0.0214	1.20	0.83	2.72
177	30	3.53	7.31	2.10	0.0232	1.44	0.69	3.02
178	20	3.88	7.33	2.11	0.0190	1.18	0.85	2.49
181	10	3.32	7.65	1.88	0.0073	.87	1.15	1.63
182	10	3.50	7.55	1.86	0.0145	.88	1.14	1.63
183	10	3.41	7.57	1.85	0.0295	.89	1.12	1.65
186	70	(3.3)	(7.1)	---	---	---	---	---
187	70	2.90	7.37	---	---	---	---	---
188^c	70	3.90	6.68	2.87	0.0718	2.45	0.41	7.0
189^c	70	3.54	6.87	2.74	0.157	2.62	0.38	7.2
190	50	3.59	7.20	2.26	0.0073	2.80	0.36	6.3
191	50	4.01	7.04	2.23	0.0177	2.31	0.43	5.2
192	50	1.13	8.16	2.59	0.0154	1.72	0.58	4.45
193	85	3.72	6.81	4.05	0.0066	2.66	0.38	10.8
196	85	3.72	6.83	3.90	0.0235	2.37	0.42	9.2
197	60	(3.84)	(7.06)	2.48	(0.0368)	(2.40)	(0.42)	(6.0)
198	95	3.71	6.73	5.12	0.0156	2.13	0.47	10.9
200	60	(3.88)	(7.04)	---	---	---	---	---
204	64.3	0	8.33	inf.	0	---	---	6.22
205	64.3	.71	8.11	4.20	0.0246	1.40	0.71	5.9
206	64.3	2.71	7.36	2.75	0.0365	2.29	0.44	6.3
207	64.3	3.86	6.93	2.60	0.0365	2.44	0.41	6.4
208	48.5	0	8.46	inf.	0	---	---	3.36
209	68.4	0	8.30	inf.	0	---	---	6.12
210	48.5	5.53	6.38	2.31	0.0295	2.18	0.46	5.0
211	68.4	(5.70)	(6.20)	2.62	0.0344	(2.63)	(0.38)	(6.9)
212^c	59.9	0.79	8.05	3.55	0.0393	1.51	0.66	5.4
213^c	59.9	3.71	7.14	2.42	0.0550	2.40	0.42	5.8
223^c	51.2	1.53	7.89	2.42	0.0464	1.84	0.54	4.45
224^c	50.5	1.00	8.05	2.57	0.0353	1.31	0.76	3.36
225	71.5	5.73	6.16	2.62	0.0331	2.82	0.355	7.4

c > 2% change in concentration of [S] or [M]. [S] and [M] corrected to average concentration.

Note-1 $[Sp] = \frac{\text{moles } SO_2 \text{ in polymer}}{\text{liter of reactant solution}}$

APPENDIX B

SAMPLE CALCULATION

Run No. 183

Experimental data:

date: 11-13-61

PRF source - center well, dewar B

reaction temperature, T	10°C
irradiation time, t	120 min.
wgt. of empty reaction tube	94.13 gm.
wgt. tube + styrene	112.29 gm.
wgt. tube bottom + styrene + SO_2	109.734 gm.
wgt. tube top	7.583 gm.
wgt. polymer, P	0.1740 gm.
sulfur analysis, wgt. % sulfur	12.51%
solubility in benzene	4%

1. Reactants

(M.W. styrene = 104.14, M.W. SO_2 = 64.07)

wgt. styrene, (M) = 112.29 - 94.13 = 18.16 gm.

wgt. SO_2, (S) = 109.734 + 7.583 - 112.29 = 5.03 gm.

moles styrene = 18.16/104.14 = 0.174 moles

moles SO_2 = 5.03/64.07 = 0.0785 moles

molar ratio, $[S]/[M] = 0.0785/0.174 = 0.45$

from Fig. IV-10, $\rho = 1.01$ gm/cm^3

volume = (18.16 gm. + 5.03 gm.)/1.01 gm/cm^3 = 23.0 ml.

$[M]$ = 0.174 moles/0.0230 liters = 7.57 moles/liter

$[S]$ = 0.0785 moles/0.0230 liters = 3.41 moles/liter

2. Dose rate

from Fig. IV-11, I = 1245 rad/min on 6-5-62

half life of Co^{60} = 5.24 years

11-13-61 to 6-5-62 = 0.54 years

0.54/5.24 = 0.10 half lives

$I_2/I_1 = 1245/I = 2^{-0.10} = 0.933$

$I = 1245/0.933 = 1330$ rad/min

Total Dose = 1330 x 120 min = 160 kilorad

3. Weight fraction yield

$P/(S + M) = 0.1740/(18.16 + 5.03) = 0.0075$

$[P/(S + M)]$/megarad = (0.0075/160 krad) x 10^3 = 0.047 megarad^{-1}

4. Polymer composition

Wgt. % SO_2 = (12.15% S) (2.0) = 25.02% SO_2

Wgt. % styrene = 100 - 25.02 = 74.98% styrene

n = moles styrene/mole SO_2 in polymer

$n = (74.98/104.14)/(25.02/64.07) = 1.85$

$1/(n-1) = 1/0.85 = 1.18$

n_o = n based on the fraction of polymer insoluble in benzene

Wgt. fraction of polymer insoluble in benze = 1 - 0.04 = 0.96

Wgt. % SO_2 in insoluble fraction of polymer = 25.02%/0.96 = 26.06%

Wgt. % styrene in insoluble fraction of polymer = 100-26.06 = 73.94%

$n_o = (73.94/104.14)/(26.06/64.07) = 1.75$

$1/(n_o-1) = 1/0.75 = 1.33$

5. Polymer molar yield

Wgt. SO_2 in polymer = (0.1740 gm. P)(0.2502 wgt. fraction SO_2)

= 0.0436 gm.

millimoles SO_2 in polymer = 0.0436/64.07 = 0.680 millimoles

$[S_p]$ = 0.680 millimoles/23.0 ml. = 0.0295 mole/l.

6. Reaction rate

$$d\,[S]/dt = [S_p]/t = 0.0295/120 = 2.46 \times 10^{-4} \text{ mole/l.-min}$$

$$\frac{-\,d[S]/dt}{[M]\;I^{1/2}} = \frac{2.46 \times 10^{-4}}{(7.57)(1330)^{1/2}} = 0.89 \times 10^{-6} \text{ rad}^{-1/2}\text{min}^{-1/2}$$

$$\frac{-\,d[M]/dt}{[M]\;I^{1/2}} = \frac{-\,d[S]/dt}{[M]\;I^{1/2}}\,n = (0.89 \times 10^{-6})(1.85)$$

$$= 1.65 \times 10^{-6} \text{ rad}^{-1/2}\text{ min}^{-1/2}$$

7. Additional functions used in graphs

$$\frac{[M]I^{1/2}}{-\,d[S]/dt} = \frac{1}{0.89 \times 10^{-6}} = 1.12 \times 10^{6} \text{ rad}^{1/2}\text{min}^{1/2}$$

$$\ln\left[(n-2)[S]\right] = \ln\,(1.85-2)(3.41) =$$

not applicable for $n < 2$

$$\ln\left[[S]\Big/\frac{2-n_o}{n_o-1}\right] = \ln\left[(3.41)\Big/\frac{2-1.75}{1.75-1}\right] = \ln 10.23$$

$$= 2.32$$

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