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## Kinetics and mechanism of the hydroperoxide initiated copolymerization of cyclohexene and sulfur dioxide.

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KINETICS AND MECHANISM OF THE HYDROPEROXIDE  
INITIATED COPOLYMERIZATION OF CYCLOHEXENE  
AND SULFUR DIOXIDE

A Dissertation Presented

by

Bernd Oster

Submitted to the Graduate School of the  
University of Massachusetts in partial  
fulfillment of the requirements for the degree of

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April

1974

Polymer Science and Engineering

KINETICS AND MECHANISM OF THE HYDROPEROXIDE  
INITIATED COPOLYMERIZATION OF CYCLOHEXENE  
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April 1974



To Mary, wife, mother and teacher, whose constant  
support made even the dark hours bright.

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## ABSTRACT

Kinetics and Mechanism of the Hydroperoxide Initiated  
Copolymerization of Cyclohexene and Sulfur Dioxide

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An equimolar charge-transfer complex formed from sulfur dioxide and cyclohexene was found to be present during the copolymerization of these monomers. The spectrophotometrically determined concentration of this complex was observed to decrease during the polymerization reaction.

The equilibrium constant of complex formation, the complex extinction coefficient and thermodynamic properties were determined in n-hexane and dichloromethane. The enthalpy of formation of the complex in dichloromethane was found to be significantly less than that in n-hexane and the extinction coefficient was significantly greater in the more polar solvent.

The copolymers formed from the reaction of sulfur dioxide and cyclohexene were found to be composed of alternating, equimolar segments, independent of comonomer composition and reaction temperature.

Negligible chain transfer to chlorinated solvents occurred during the polymerization reaction.

Copolymers of 50,000 number average molecular weight and 1.6 polydispersity ratio,  $\overline{M}_w/\overline{M}_n$ , were prepared at temperatures below  $-30 \pm 3^\circ\text{C}$ . The number average molecular weight decreased five-fold and the polydispersity ratio increased by a factor of two when polymerization was carried out above this temperature. The change in molecular weight and distribution occurred over a very limited temperature range and negligible variation of molecular weight and distribution with temperature was found at temperatures above and below this range.

Initiation of the copolymerization did not occur spontaneously, i.e., without the addition of initiator, when purified cyclohexene was used. Spontaneous polymerization occurred, however, when the unpurified monomer was employed. Initiation of the copolymerization could be brought about by the addition of hydroperoxides, whereas peroxides and other free-radical initiators were not effective at the low experimental temperatures.

The hydroperoxide initiator was found to decompose both homolytically and heterolytically in the presence of sulfur dioxide. The heterolytic decomposition reaction produced a peroxide and sulfuric acid. The presence of sulfuric acid during the polymerization caused a surface coloration of the

polymer presumed to be due to the cationically catalyzed oligomerization of trace amounts of olefins. The occurrence of two competing initiator decomposition reactions was found to cause the polymerization reaction to stop prior to the exhaustion of the comonomers.

Polymerization rate data was obtained from measurement of sulfur dioxide concentration and charge-transfer complex optical density. The reversibility of the propagation reaction was confirmed. The reaction rate data was found to fit a kinetic model based on propagation of the chain reaction by alternate addition of the comonomers. A model assuming propagation by addition of the charge-transfer complex did not fit the data.

Based on the magnitude of the molecular weight distribution ratio,  $\bar{M}_w/\bar{M}_n$ , of polymers prepared below  $-30^\circ\text{C}$ , termination of the copolymer chain was determined to occur by combination rather than by disproportionation. A model in which it was assumed that combination of two sulfonyl radicals controls the termination reaction was found to fit the experimental data.

The combination of polymerization reaction rate constants  $k_2(fk_d/k_{tSS})^{\frac{1}{2}}$  was found to equal  $0.00013 \pm 0.0002$   $\text{l mol}^{-1}\text{sec}^{-1}$  at  $-19^\circ\text{C}$ . The activation energy of the overall polymerization reaction was estimated to equal 8 kcal/mole. A pseudo-first order rate constant for the



sulfur dioxide-induced homolytic decomposition of t-butyl hydroperoxide was found to equal  $0.9 \pm 0.2 \text{ sec}^{-1}$  at  $-19^{\circ}\text{C}$ . The activation energy of this decomposition reaction was evaluated to be  $8.6 \pm 4.3 \text{ kcal/mole}$ . Heterolytic decomposition of the initiator was found to proceed much more rapidly than the homolytic decomposition reaction and to be only slightly temperature dependent.

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## I. INTRODUCTION

### Ia. Objective and Scope

Since the proposal by Barb in 1952<sup>1</sup> that a charge-transfer complex formed from an electron donor and an electron acceptor monomer acted as the propagating species in the copolymerization of styrene and sulfur dioxide, many investigations have been undertaken to clarify the role of the complex in the copolymerization of monomers of differing polarities. No completely satisfactory proof of the participation of the complex has yet been reported. The objective of the present investigation was to determine whether this mechanism could be confirmed using the technique of following the course of the reaction by spectrophotometric observation of the charge-transfer complex concentration and chromatographic determination of monomer concentrations. Examination of the compositions, molecular weights and molecular weight distributions of copolymers produced in these studies was undertaken to amplify and confirm the kinetic analysis of the rate data.

To achieve this end, cyclohexene and sulfur dioxide were chosen as the comonomers principally because neither of these monomers are known to form homopolymers, simplifying analysis of the rate data, and because the copolymer formed was readily soluble in a convenient solvent.

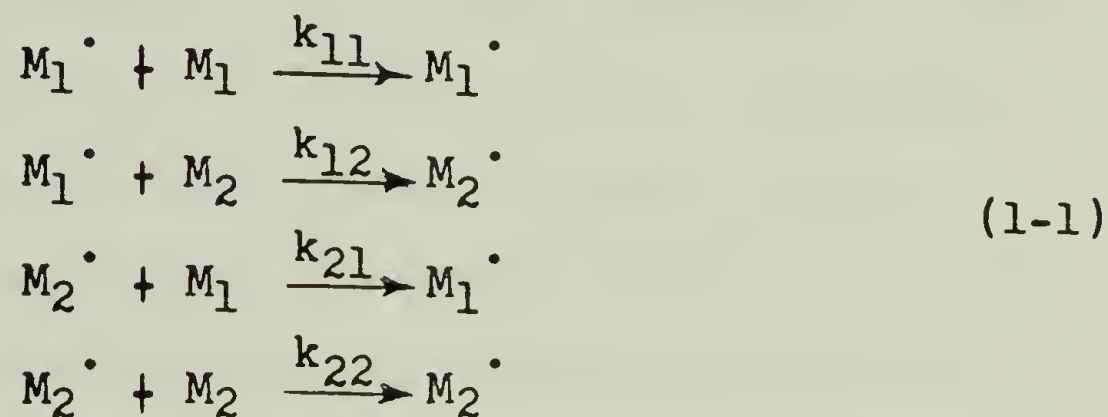
Dichloromethane was chosen as a solvent because of its transparency, required for spectrophotometric studies, the complete solubility of both monomer and copolymer in this solvent, and because of its low freezing point. Temperature range of this investigation was dictated by the requirement that the known reversibility of the polymerization reaction be minimized, that the charge-transfer complex concentration be maximized, and that volatilization of sulfur dioxide be negligible. Based upon these requirements, it was decided to carry out the majority of the experiments at temperatures between  $-20$  and  $-50^{\circ}\text{C}$ . This range of experimental temperatures limited the choice of polymerization initiators to a system which would be effective at low temperature. The sulfur dioxide induced decomposition of hydroperoxides was found to be the only practical reaction to achieve efficient formation of free radicals at the experimental temperatures, and *t*-butyl hydroperoxide was used to initiate the polymerization reaction. Although this choice of initiator introduced a competing initiator-decomposition reaction into the mechanism, complicating analysis of the data, it permitted the estimation of rate constants of both initiator decomposition reactions from the polymerization rate data.

In connection with the kinetic study of the polymerization reaction, the extinction coefficient and equilibrium

constant of the sulfur dioxide-cyclohexene charge-transfer complex were determined.

### Ib. Charge-Transfer Complex Copolymerization

Introduction. The effect of monomer polarity and, to some extent, resonance stabilization in controlling the degree of randomness of the structure of copolymers has long been recognized. The equations describing irreversible propagation of copolymerization without penultimate effect are:



and the probability of any two segment sequence is given by the quotient of the probability of a molecule reacting to form a reactive chain end to the total probability of obtaining that reactive chain end. Thus,

$$P_{11} = k_{11} [M_1^\cdot] [M_1] / (k_{11} [M_1^\cdot] [M_1] + k_{12} [M_1^\cdot] [M_2]) \tag{1-2}$$

Defining the monomer reactivity ratios as  $r_1 = k_{11}/k_{12}$  and  $r_2 = k_{22}/k_{21}$ , the binary sequence probabilities are:



$$\begin{aligned}
 P_{11} &= r_1 [M_1] / (r_1 [M_1] + [M_2]) \\
 P_{12} &= [M_2] / (r_1 [M_1] + [M_2]) \\
 P_{21} &= [M_1] / ([M_1] + r_2 [M_2]) \quad (1-3) \\
 P_{22} &= r_2 [M_2] / ([M_1] + r_2 [M_2])
 \end{aligned}$$

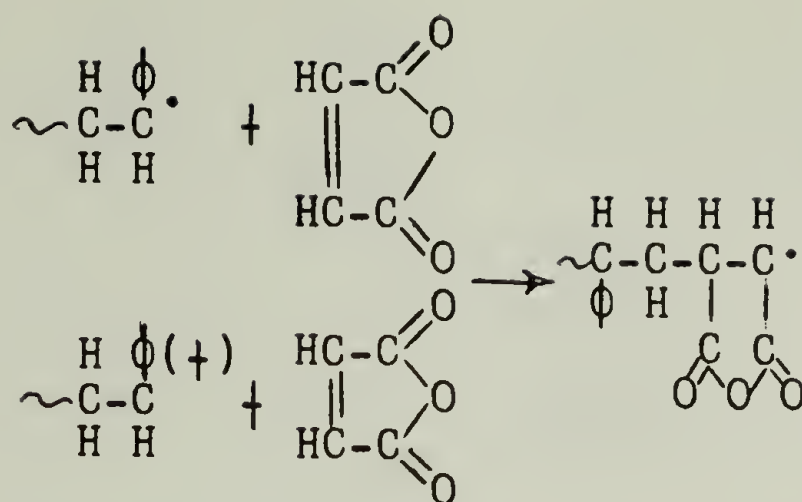
In the limiting cases, for a completely random copolymer  $P_{11}=P_{12}=P_{21}=P_{22}=0.25$  and  $r_1 r_2=1$ ; for a perfectly alternating copolymer  $P_{11}=P_{22}=0$ ,  $P_{12}=P_{21}=1$ , and  $r_1=r_2=0$ . Thus the alternating tendency for pairs of comonomers increases as the reactivity ratio product decreases to zero. The products of the reactivity ratios have been found to decrease as the difference in polarity of the comonomers increases. For example, the electron acceptor monomer acrylonitrile forms fairly alternating sequences with the electron donor butadiene ( $r_1 r_2 = 0.02$ ) but random sequences with the electron acceptor methyl acrylate ( $r_1 r_2 = 1$ ).<sup>2</sup> Increasing the difference in comonomer polarity increases the rate of radical addition.<sup>3</sup> This has been attributed to mutual polarization of monomer and radical as they approach each other in the transition state, stabilizing it. An alternate model, a change in the charge distributions of monomer and radical in the ground state, would lead to the dependence of reactivity on the dielectric constant of the medium which is normally not observed.<sup>4</sup>

With monomer pairs of very different polarities (e.g. styrene-maleic anhydride, olefin-sulfur dioxide), the

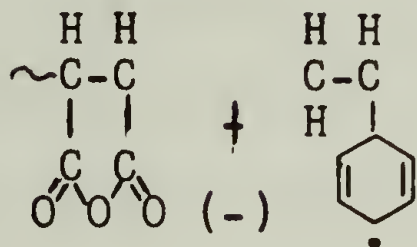
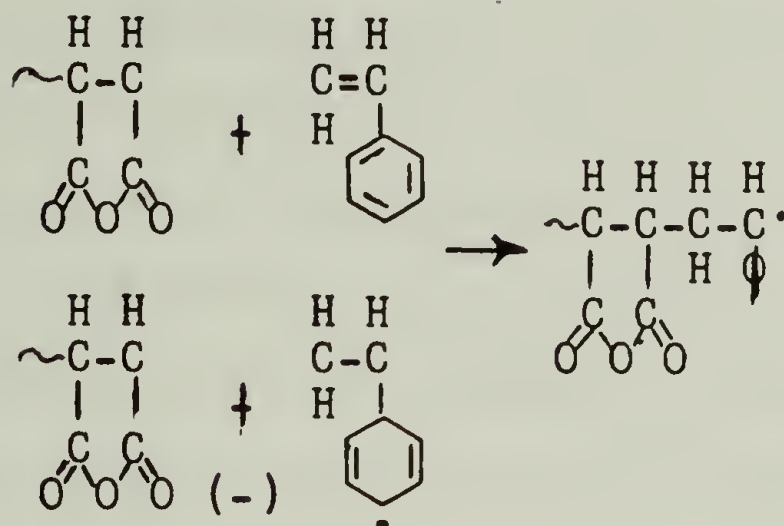


one electron transfer between electron-donor monomer and electron-acceptor monomer leads to the formation of a distinct, low molecular weight chemical entity, a charge-transfer complex. During the copolymerization of such monomer pairs, visible or ultraviolet charge-transfer light absorption bands are usually observed. Increased reactivity, anomalous solvent effects and anomalous effects in terpolymerizations containing donor-acceptor monomer pairs have been attributed to participation of the charge-transfer complex as a separate entity, i.e. as a single monomer unit.

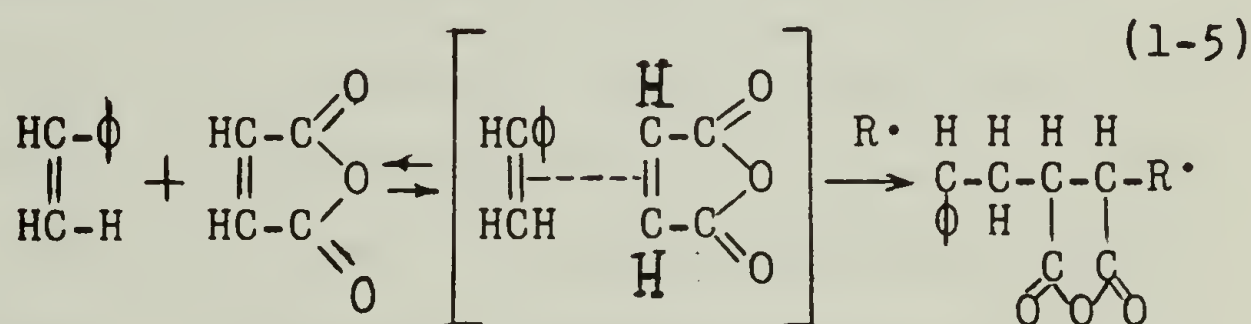
However, alternate reaction paths have also been suggested for the free radical copolymerization of donor-acceptor pairs. In the first mechanism, enhanced reactivity is attributed to stabilization of the transition state between radical and monomer by electron transfer to produce resonance structures.<sup>4</sup> Two of the resonance structures possible for the monomers and growing chains are illustrated in Equation (1-4) for the copolymerization of styrene and maleic anhydride.



(1-4)

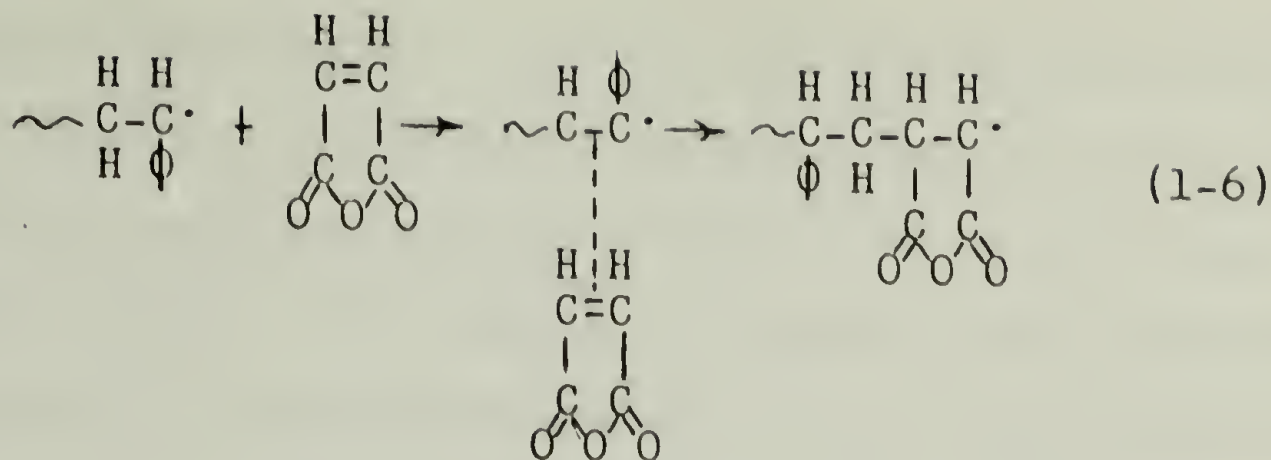


The charge-transfer complex propagation mechanism ascribes the increased reactivity to the more highly energetic charge-transfer complex. <sup>5</sup>



(1-5)

In an intermediate interpretation, Equation (1-6), the energy of the transition state is decreased by the formation of a complex between the polymer radical and a comonomer of opposite polarity. <sup>6</sup>



Ibl. Solvent effect. The participation of a complex of monomers of dissimilar polarity in some manner in copolymerization may be indicated by the effect of dielectric constant of the medium, which does not influence the course of polymerization of two monomers of similar polarity. Charge-transfer complex stability invariably decreases as the dielectric constant of the medium increases.<sup>7</sup> Additionally, formation of a charge-transfer complex between a solvent and one of the comonomers can result in a decreased concentration of the complex between the comonomers. Solvents of increasing dielectric constant were shown to decrease the rate of copolymerization of maleic anhydride and vinyl isobutyl ether.<sup>6</sup> Increasing polymerization rate with a change in comonomers composition was correlated with a decrease in the dielectric constant of the comonomer mixture by Hallensleben.<sup>8</sup> Competition between a pyridine-sulfur dioxide complex and a styrene-sulfur dioxide complex was cited by Matsuda and Iino as the cause of increased polystyrene concentration when pyridine was used as a solvent in the styrene-sulfur dioxide copolymerization.<sup>9</sup>



The solvent-induced anomalies in the polymerization rates could be attributable to solvent interactions in the initiation reaction instead of the effect on the charge-transfer complex. The effect of solvent on the copolymer composition in the styrene-sulfur dioxide copolymerization may be due to the enhanced tendency toward cationic homopolymerization, as described by Barb<sup>1</sup> and Herz et al.,<sup>10</sup> occurring in solvents of higher dielectric constant.

Ib2. Terpolymerization behavior. Terpolymerization of two electron acceptor monomers has been shown to produce polymers containing 50% acceptor units regardless of starting monomer composition.<sup>11</sup> Terpolymerization of a donor and an acceptor monomer and one of intermediate polarity produced terpolymers containing a constant ratio of donor to acceptor polymer units.<sup>12</sup> These results have been interpreted as being due to copolymerization of two complexes in the first instance and being due to copolymerization of a complex with a third monomer in the second. Terpolymerization experiments do, indeed, show that a strong interaction between electron donor and acceptor molecules influences the course of the reaction, but do not clarify whether this interaction occurs by the formation of a complex or by preferential addition of a monomer unit of opposite polarity to the growing chain.

Ib3. Chain transfer. The absence of a chain transfer effect of  $\text{CCl}_4$  in alternating copolymerizations was

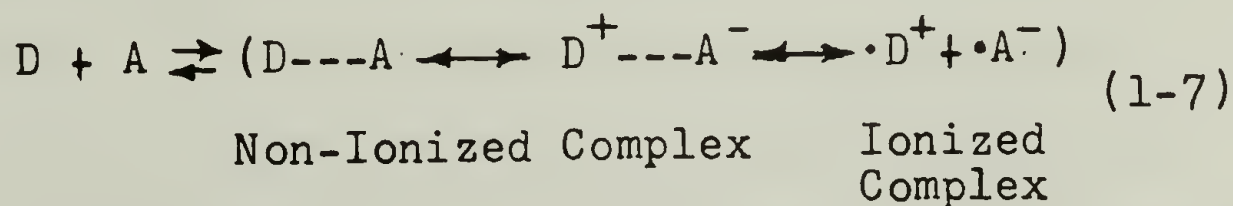


discussed by Hirooka.<sup>13</sup> He ascribed this behavior to the dipolar repulsion between the chain transfer agent and the acceptor monomer and consequent inability of these two species to react. The absence of any reaction between the electron donor and the chain transfer agent was attributed to the nonparticipation of the donor radicals in copolymerization, i.e., propagation via the complexed monomers with only acceptor endgroup radicals.

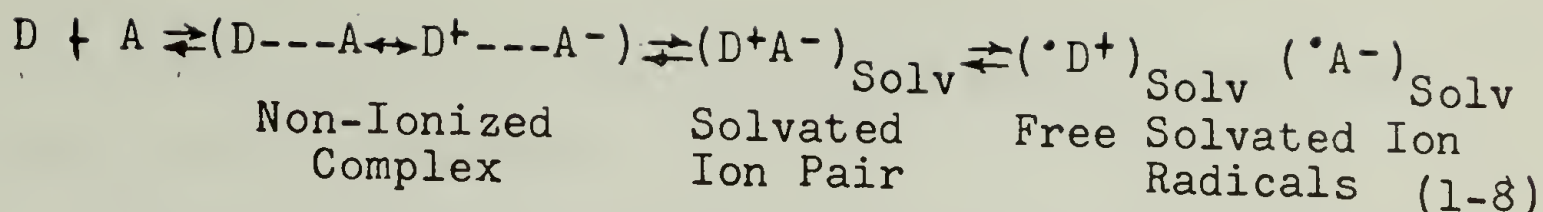
Ib4. Complexed copolymerizations. Alternating copolymerizations between electron donor monomers and vinyl compounds in which conjugated nitrile or carbonyl groups are complexed with metal halides have been reported.<sup>14</sup> The analogy between these copolymerizations and alternating donor-acceptor copolymerizations was discussed by Hirooka.<sup>13</sup> The formation of a complex between the carbonyl or nitrile functionality and the metal halide increases the electron acceptor character of these normally weak electron acceptors. Metal halide complexation of the vinyl monomers results in the formation of exactly alternating copolymers from monomers which would normally produce random copolymers, and permits the copolymerization of allylic monomers which would not copolymerize with uncomplexed vinyl monomers due to the unreactivity of the allylic radical. Hirooka demonstrated that complexed polymerization proceeds by a free radical mechanism and that both the stability of the metal halide-vinyl monomer complex and the electron

donor capacity (or degree of conjugation) of the donor monomer determine whether random or alternating copolymerization takes place.

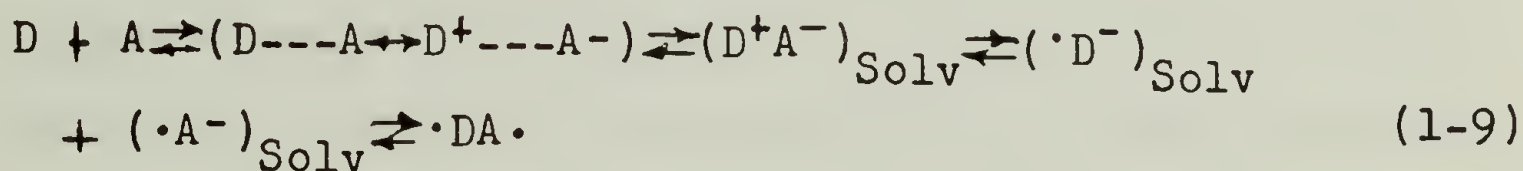
Ib5. Initiation by charge-transfer complex. Initiation of addition polymerization occurs when a monomer molecule acquires a pair of electrons (anionic initiation), donates an electron pair (cationic initiation) or gains or loses a single electron (free-radical initiation). The first active chain segment is usually formed by reaction with another active ion or radical (e.g. reaction with the dissociated anion of an organometallic compound to form monomer anions or homolytic decomposition of a peroxide followed by addition of the radical formed to a monomer molecule). The initial active entity may also result from the direct interaction of the monomer with a non-active substance to produce an active species by electron interchange. This can occur if a charge-transfer complex is formed in which an increasing degree of charge separation can eventually lead to the formation of radical ions:



and where further charge separation of the non-ionized complex may occur by solvation: <sup>15</sup>



The initiation of cationic polymerization of strong electron donor monomers, mainly N-vinyl carbazole, by cation radicals formed from the charge-transfer complex of the monomer with strongly electrophilic additives has been reviewed by Ellinger.<sup>15</sup> Electron transfer, charge separation by solvation and combination of ion radicals in the weaker charge-transfer complexes formed by donor and acceptor monomers may lead to the formation of biradicals which initiate the copolymerization as indicated in Equation (1-9).



Initiation of copolymerization by biradicals formed from charge-transfer complexes was discussed by Gaylord,<sup>5</sup> while the inefficiency of biradicals in initiating polymerization due to the tendency of short biradical chains toward termination by cyclization was pointed out by Walling.<sup>16</sup> Pryor discussed the participation of 1, 4 biradicals in the spontaneous thermal initiation of styrene polymerization.<sup>17</sup> Nevertheless, the mechanism of initiation by the charge-transfer complexes formed from electron donor and acceptor monomers or even the fact that



such "spontaneous" initiation occurs has not yet been definitively established.

#### Ic. The Electron Donor-Acceptor Charge-Transfer Complex

Introduction. Intensive investigation of the properties and behavior of organic charge-transfer complexes has been undertaken since 1949 when Benesi and Hildebrand reported that solutions of aromatic hydrocarbons and iodine had an absorption band not present in solutions of either compound alone.<sup>18</sup> A large number of reviews and books have been written dealing with both general and specific aspects, such as theoretical descriptions,<sup>7,19,20,21</sup> and reactions of the complexes.<sup>22</sup> To provide a background for a study of the involvement of charge-transfer complexes in copolymerization, a description of the nature of the complexes, their behavior and experimental methods used in detection is given in this section.

Icl. Definition of complexes. A complex may be considered to be an association of atoms which cannot be adequately described in terms of classical covalent or ionic bonding. The intermolecular interactions contributing to the formation of the complex are usually stronger than van der Waal's forces and are of such a character as to preclude their description in terms of these forces. A complex may be identified as being a substance, formed by



the interaction of two or more component molecules, which may have an independent crystal structure, and which will dissociate reversibly into its component molecules in solution or in the vapor state.

Definition of charge-transfer complex. In the charge-transfer complex, the intermolecular forces are due to weak interactions between an electron donor and an electron acceptor which may involve an actual transfer of an electron from an electron donor to the electron acceptor. These complexes are composed of simple integral ratios of electron donor and acceptor molecules and have very fast rates of formation and decomposition, making it appear that the complexes are formed instantaneously. Their enthalpy of formation is on the order of one to ten kcal/mole. A prominent characteristic of the complexes is the appearance of electronic absorption bands in addition to those of the components.

Electronic absorption spectra of charge-transfer complexes. The excitation of an electron to a higher energy level by a photon gives rise to energy absorption in the ultraviolet and visible regions of the spectrum. This electron excitation of a charge-transfer complex by radiation involves the complete or partial transfer of an electron from one component of the complex to the other. A valence bond description of the electronic absorption in terms of intermolecular charge-transfer transitions was

developed by Mulliken. <sup>21</sup> Based on this theory, therefore, bonding between the electron donor and acceptor in the ground state is due chiefly to van der Waal's interactions with a small, though definite, contribution from charge-transfer of an electron from donor to acceptor. In the excited state the predominant structure is that involving the complete transfer of an electron. The absorption spectrum is due to transitions between these states. In addition to the absorption due to electron transfer in the complex, charge-transfer transitions can occur during the random collision of donor and acceptor molecules. The observed strong charge-transfer bands exhibited by weakly associated pairs, e.g. aliphatic hydrocarbon-iodine, has been attributed to random contact charge-transfer transitions. <sup>21</sup>

Donor and acceptor types. Mulliken classified both donors and acceptors as being of either increvalent or sacrificial character. Increvalent donors are lone pair (n) donors such as aliphatic amines, alcohols or iodides. Increvalent acceptors are of the vacant orbital (v) type (e.g.  $\text{BF}_3$ ,  $\text{SnCl}_4$ ). Sacrificial donors donate electrons from a bonding orbital. These include very weak donors which donate electrons from a sigma bond (e.g. aliphatic hydrocarbons) and much more strongly electron releasing pi donors such as aromatic compounds and olefins. Sacrificial sigma electron acceptors include the hydrogen halides,

halogens and halosubstituted aliphatic compounds, while sacrificial pi acceptors, the most common organic acceptors, are aromatic compounds with electron withdrawing substituents or aromatic cations. Bonding in the charge-transfer complex can have the  $sp^3$  character of a sigma bond, or it can be through pi bonding in which the resonance energy of the components is decreased only slightly, or it can involve bonding by a lone pair electron of the donor.

The stability of complexes as indicated by their enthalpies of formation ranges from 10 kcal/mole for complexes of increvalent donors with increvalent acceptors (e.g.,  $BF_3$ -ethyl ether), to 3-15 kcal/mole for complexes of increvalent donors with sacrificial acceptors (e.g., carbonyl compounds-iodine), to 1-4 kcal/mole for sacrificial donor-sacrificial acceptor complexes (e.g., benzene-iodine) to less than 2 kcal/mole for sacrificial donors complexed with increvalent acceptors (e.g., benzene-carbon tetrachloride).<sup>23</sup>

#### Ic2. Characterization of charge-transfer complexes.

Complex formation may be demonstrated, its stoichiometry determined, the equilibrium constant measured and, if the complex is sufficiently stable, the complex may be isolated by a number of physico-chemical methods. For relatively stable complexes, non-spectrophotometric methods may be used to determine equilibrium constants. These include the following:<sup>24</sup> (1) solubility measurements which involve



the determination of the increased solubility of a compound in a solution containing another compound of opposite electron interchange characteristics; (2) distribution studies in which the equilibrium constant is determined from partition of a compound between two phases after equilibrium extraction with a solution of opposite electron interchange characteristics; (3) the deviation from ideality of the measured vapor pressure of mixtures of electron donors and acceptors in which the concentration at which the maximum deviation occurs indicates the stoichiometry of the complex, and the magnitude of the deviation may be used to calculate the thermodynamic constants of complex formation; (4) melting point-composition diagrams in which the stoichiometry of the complex is determined from the appearance of maximum melting eutectic points; (5) measurement of dipole moment, conductance and viscosity which indicate the stoichiometry of complexes by deviation of these properties from ideality; (6) direct calorimetry in which the enthalpy of formation is measured directly; and (7) kinetic studies of a reaction of the complex which may be used to calculate the equilibrium constant of complex formation.

Nuclear magnetic resonance. Although electron spin resonance and nuclear quadropole resonance studies of complexes have been undertaken, the use of nuclear magnetic resonance in the determination of complex equilibrium



constants is the most common application of resonance techniques in this field. The position of the magnetic resonance of a nucleus represents a time-averaged resultant of its behavior in different environments when the molecular environment of the nucleus is changing rapidly and reversibly. By measuring the change in chemical shift of a nuclear resonance of the acceptor, for example, as a function of added donor concentration, the equilibrium constant may be determined. This is accomplished by the application of two equations as follows:

(a) the definition of the chemical shift in terms of its values in different environments:

$$(\delta - \delta_A) \equiv \Delta = P_{AD}(\delta_{AD} - \delta_A) \equiv P_{AD} \Delta_o \quad (1-10)$$

where  $\delta$  is the observed chemical shift,  $\delta_A$  is the chemical shift of the pure acceptor,  $\delta_{AD}$  is the chemical shift of the complex and  $P_{AD}$  is the fraction of the acceptor molecules uncomplexed, and

(b) the definition of the equilibrium constant (for an equimolar complex):

$$K_c = [X] / (([A]_o - [X]) ([D]_o - [X])). \quad (1-11)$$

where  $K_c$  is the equilibrium constant in terms of molar concentrations, and  $[X]$ ,  $[A]_o$  and  $[D]_o$  are the molar concentrations of the complex, acceptor and donor, respectively. If one of the components, the donor for instance, is in large excess, these equations may be solved simultaneously

to yield a relationship between the donor concentration and the observed chemical shift from which the equilibrium constant and the chemical shift of the complex relative to the acceptor may be calculated.

Infrared spectroscopy. Changes in intensity and energy of vibrational bands of the components may occur upon complex formation. These changes are generally slight and are associated with the components rather than the complex. Decreases in the vibrational frequencies associated with both donor and acceptor molecules due to the presence of a complex are sometimes observed.

Electronic absorption spectroscopy. The most practical and most widely applied method characterizing charge-transfer complexes is that of electronic absorption spectroscopy. Several reasons are apparent for the extensive use of this method. Simple ultraviolet or visible spectrophotometers may be used. Since the extinction coefficients of charge-transfer complexes are usually high, determinations may be made at very low concentrations where ideal solution behavior is observed and where simplified procedures may be used for the evaluation of constants. This advantage of the method may, at times, become a disadvantage in that impractically thin optical cells may be required to perform measurements at higher concentrations. The wavelength of the charge-transfer absorption is a

direct measure of the energy of the transition between ground and excited states and is empirically and theoretically relatable to the electron interchange characteristics of both components, i.e., the ionization potential of the donor and the electron affinity of the acceptor.

Stoichiometry of complex. The molecular relationship between the two components of a complex may be obtained by the method of continuous variations.<sup>27</sup> In this procedure a property of the complex is measured as a function of concentration of the components. The concentration at which a maximum in the property occurs is relatable to the stoichiometric ratio of the two components. In the normally used application of this method it is assumed that the complex concentration is much less than that of the components so that the general equilibrium relationship:

$$K_c = cw / ([A]_0 - cw)([D]_0 - cw)^n \quad (1-12)$$

may be simplified to:

$$c = (K_c/w)[A]_0[D]_0^n \quad (1-13)$$

If the system consists only of the two components of the complex:

$$c = (K_c/w)[A]_0(1 - [A]_0)^n \quad (1-14)$$

and the maximum value of the property, obtained by equating the first derivative of the property to zero, equals:

$$[A]_{0\max} = 1/(1+n) \quad (1-15)$$



where  $K_c$  is the equilibrium constant of the reaction:



$n$  is the molar ratio of components in the complex,  $[A]_0$  and  $[D]_0$  are the molar concentrations of the components as charged,  $w$  is a property of the complex and  $c$  is a proportionality constant between the property and the molar complex concentration. In applying this method to absorption spectrophotometric measurements the proportionality constant,  $c$ , equals the product of complex extinction coefficient,  $\epsilon_c$ , and optical path length,  $l$ , obtained from the Beer-Lambert law:

$$\log(I_0/I) = OD = \epsilon_c l [X] \quad (1-17)$$

where  $OD$  is the measured optical density,  $I_0$  is the intensity of incident light, and  $I$  is the intensity of light transmitted through the solution, and  $[X]$  is the molar concentration of the complex.

Complex equilibrium constant, extinction coefficient and thermodynamic constants. The determination of the complex equilibrium constant and the extinction coefficient is based upon the equilibrium relationship between the concentrations and the Beer-Lambert law. The equations written below apply to ideal solution behavior (i.e. unit activity coefficient), equimolar stoichiometric ratio of donor and acceptor in the complex and a one cm optical path



length. They may be modified by substituting activities for molar concentrations, rederiving the equations based on the actual stoichiometric ratios and substituting  $OD/l$  for the optical density if an optical path length other than one cm is used.

The most commonly used equations and their regions of applicability are the following:

(a) the Benesi-Hildebrand equation which is used if one component (the donor in the equation below) is in large excess and if neither of the two components absorb appreciable light at the wavelength of measurement:

$$\frac{[A]_0}{OD} = \frac{1}{K_c \epsilon_c [D]_0} + \frac{1}{\epsilon_c} \quad (1-18)$$

(b) the Ketelaar equation which is used under the same concentration restriction as above if absorption by the component not in excess is appreciable:

$$\frac{[A]_0}{\Delta OD} = \frac{1}{K_c \Delta \epsilon [D]_0} + \frac{1}{\Delta \epsilon} \quad (1-19)$$

where  $\Delta \epsilon$  is the difference in extinction coefficients between the complex and the light absorbing component and  $\Delta OD$  is the difference in optical density between the measured solution and a solution of the absorbing component at the same concentration in the absence of a complex.

(c) the Rose-Drago equation in which neither concentration nor optical absorption restrictions apply:

$$\frac{1}{K_c} = \frac{\Delta OD}{\Delta \epsilon} - [A]_o - [D]_o + \frac{[A]_o [D]_o \Delta \epsilon}{\Delta OD} \quad (1-20)$$

where  $\Delta \epsilon$  and  $\Delta OD$  are defined as above, except that the differences between the complex or measured values and both components apply.

Experimentally, evaluation of the complex equilibrium constant and extinction coefficient is performed by determining the optical density of solutions prepared at varying concentrations of the components. If the donor is in large excess and the restrictions of the Benesi-Hildebrand equation holds, a plot of  $[A]_o / OD$  vs.  $1 / [D]_o$  will be linear with a slope equal to  $1 / K_c$  and an intercept of  $1 / \epsilon_c$ . Similarly, a plot of  $[A]_o / \Delta OD$  vs.  $1 / [D]_o$  will be linear under the restrictions of the Ketelaar equation. In the latter case the extinction coefficient, obtained from the equation by graphical means or by linear bivariate regression analysis, equals the difference of the coefficients of the complex and that of the acceptor. Values of  $\Delta OD$  are obtained from the measured value of optical density and, by calculation, from the previously determined extinction coefficient of the acceptor and the known concentration of acceptor under experimental conditions. If no concentration restrictions exist, solution for the constants (i.e.,

in the Rose-Drago equation) involves a trial and error procedure or bivariate non-linear regression analysis.

If the complex concentration is much less than that of the components (i.e., if negligible association of the components occurs) a simple relationship which applies at high concentrations of the components and at any complex stoichiometry may be derived:

$$X = K_c [A]_o [D]_o^n \quad (1-21)$$

The empirical equation:

$$OD = (\text{constant}) \cdot [A]_o^m D_o \quad (1-22)$$

removes the restriction of applicability of the Beer-Lambert law when negligible association occurs.

The free energy, enthalpy and entropy of complex formation are determined from the equilibrium constants evaluated at a number of temperatures by applying the van't Hoff equation:

$$K_c = \exp (-\Delta F^0/RT) = \exp (-\Delta H^0/RT + \Delta S^0/R) \quad (1-23)$$

Ic3. Experimental determinations involving sulfur dioxide. Seyer and King determined the freezing points of mixtures of cyclohexene and sulfur dioxide but they failed to find a maximum in the freezing point-concentration relationship which would indicate the existence of a complex.<sup>29</sup> However, the absence of an observed eutectic composition may be attributable to the low degree of association of this system ( $K_c = 0.05$ ). Andrews and Keefer



measured the wavelength dependence of the optical density of sulfur dioxide in various concentrations of aromatic compounds dissolved in  $\text{CCl}_4$  at  $25^\circ\text{C}$ .<sup>30</sup> Attributing the enhanced optical density to equimolar complexes, they calculated the equilibrium constant and extinction coefficients of complex formation using the Benesi-Hildebrand equation, modified by an iterative procedure to account for the optical absorption of the sulfur dioxide. Their results showed that the stability of aromatic-sulfur dioxide complexes increased with electron donating ability of the ring substituents. The wavelength at which the absorption maxima occurred was found to increase with increasing methylation of the ring from 280 nm for the benzene complex to 305 nm for the mesitylene complex. An enhanced absorption maximum for the system cyclohexene-sulfur dioxide in  $\text{CCl}_4$  was found at 292 nm, close to the maximum absorption of pure sulfur dioxide at 290 nm. The investigators suggested that, due to the proximity of the enhanced and the acceptor absorption maxima, the enhanced absorption may be attributable to a sulfur dioxide transition intensified by the presence of the complex. Speculating as to the structure of aromatic-sulfur dioxide complexes, the authors proposed that the preferable structure would be one in which the sulfur dioxide atom lies above the plane of the ring with the sulfur atom closest to the ring.



The equilibrium constants and thermodynamic functions of anthracene-sulfur dioxide complex formation were determined by Tokura, et al..<sup>31</sup> Matsuda, et al.<sup>32</sup> reported the stoichiometry and the thermodynamic properties of the styrene-sulfur dioxide complex, while de Maine<sup>33</sup> measured the equilibrium constant of *n* donors (e.g., alcohols and ethers) and aromatic compounds complexed with sulfur dioxide.

The most comprehensive investigation of properties of sulfur dioxide charge-transfer complexes was performed by Booth, Dainton and Ivin.<sup>34</sup> In their spectrophotometric study, the sulfur dioxide charge-transfer complex equilibrium and thermodynamic constants of eight olefins and three aromatic compounds were determined in *n*-hexane. Equilibrium constants at 25°C of the olefins ranged from 0.037 l/mol for cyclopentene to 0.19 for 2,3-dimethyl-2-butene. The absorption spectra showed two maxima. A band whose position correlated with the ionization potential of the olefin was attributed to a transition of a charge-transfer complex. The other band, whose absorption wavelength occurred at approximately 296 nm, was attributed to enhanced absorption of the sulfur dioxide transition at 290 nm due to the proximity of a donor molecule. These investigators pictured the complex as one in which the plane of the carbon atoms makes a small angle with the plane of the sulfur dioxide molecule and in which the

sulfur atom is located symmetrically with respect to the C=C bond.

Representative charge-transfer equilibrium constants for several sulfur dioxide-electron donor systems and cyclohexene-electron acceptor systems as well as for some systems containing maleic anhydride as an acceptor are collected in Table I. Empirically, low charge-transfer complex association constants appear to be characteristic of monomer pairs which form alternating copolymers.

#### Id. Copolymerization of Sulfur Dioxide with Unsaturated Hydrocarbons

Introduction. The reaction of sulfur dioxide with unsaturated hydrocarbons involves both an addition to the double bond and an increase in valence of sulfur from 4 to 6.<sup>38</sup> In this reaction two new sigma bonds are formed which originate from the  $\pi$  electrons of the carbon-carbon double bond and the  $\pi$  electrons of the sulfur-oxygen bond. The double bond character of the sulfur-oxygen bond in sulfur dioxide is converted into the completely semipolar bonding in the resulting sulfone.<sup>39</sup>

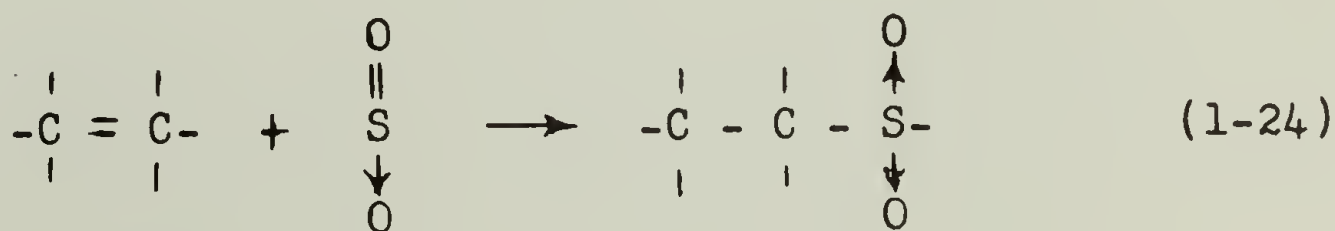
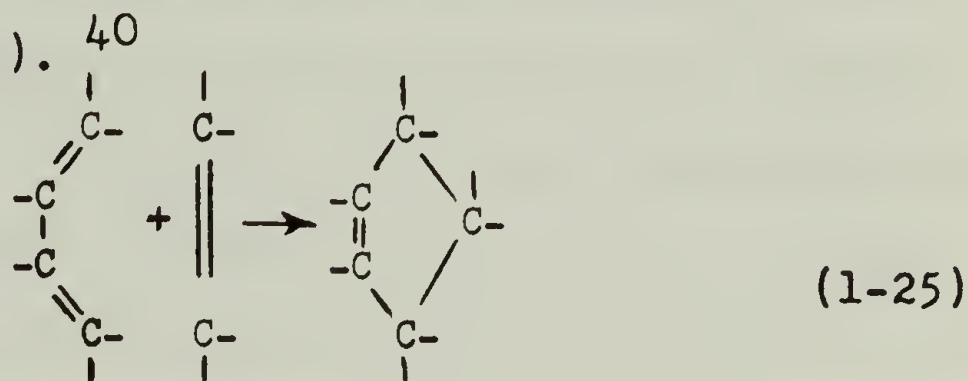


TABLE I  
Charge-Transfer Complex Equilibrium Constants  
for Various Donor-Acceptor Pairs at Room Temperature

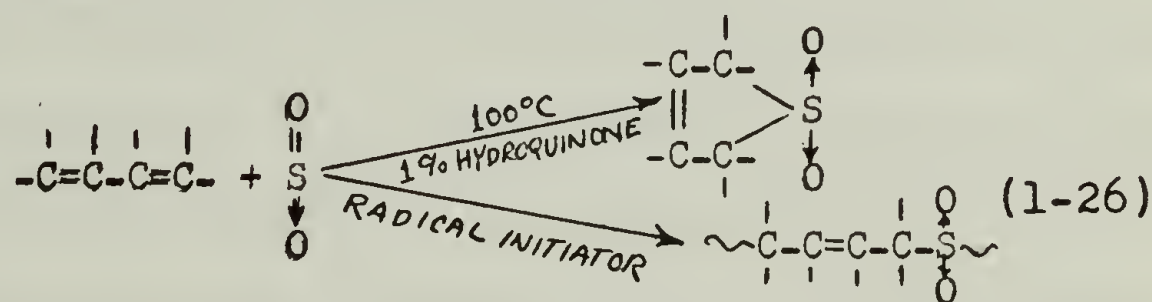
Acceptor	Donor	Solvent	$K_c, \text{l/mole}$	Reference
Sulfur Dioxide	Cyclohexene	$\text{C}_6\text{H}_{14}$	0.05	34
Sulfur Dioxide	Styrene	$\text{CHCl}_3$	0.05	32
Sulfur Dioxide	Anthracene	$\text{CCl}_4$	0.3	31
Sulfur Dioxide	Tetramethylamine	$\text{C}_7\text{H}_{16}$	2550	35
Iodine	Cyclohexene	$\text{C}_7\text{H}_{16}$	0.3	36
Silver ( $\text{Ag}^+$ )	Cyclohexene	$\text{H}_2\text{O}$	80	34
Maleic Anhydride	Styrene	$\text{CCl}_4$	0.2	37
Maleic Anhydride	DMDS*	$\text{CDCl}_3$	0.1	37
Maleic Anhydride	Divinyl ether	$\text{CDCl}_3$	0.04	37
Maleic Anhydride	Fumaronitrile	$\text{CDCl}_3$	0.008	37

\* Dimethyl Divinyl Silane

The reaction is analogous to the Diels-Alder addition of an unsaturated molecule (usually containing electron accepting substituents in conjugation with the double bond) to a diene. This reaction also involves the reorganization of electron density in which two double bonds are converted to two new single bonds, and in which the electron distribution of the moieties is altered (by the formation of a new double bond).<sup>40</sup>



The addition of sulfur dioxide to the hydrocarbon double bond may lead either to the formation of a cyclic monomeric sulfone or to the polysulfone:

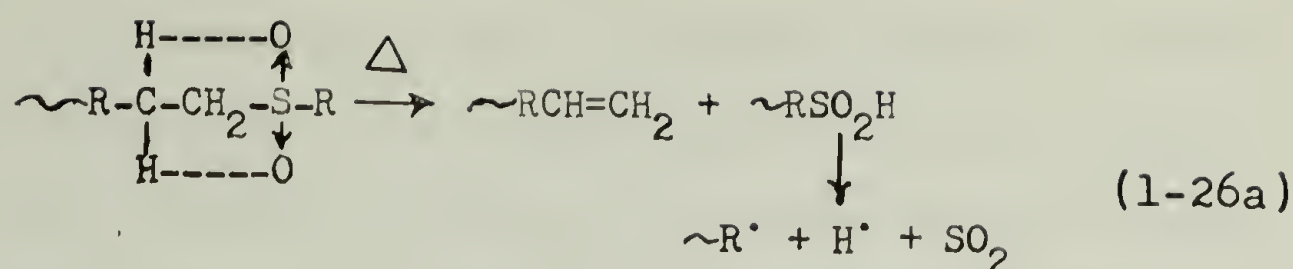


The cyclic sulfone results from the reaction of sulfur dioxide and dienes from which a stable 5 or 6 membered ring can be formed after addition.<sup>38</sup> The analogy to the Diels-Alder reaction in the formation of cyclic compounds is evident. Since even in reactions with dienes, the tendency toward polymer formation is great, radical inhibitors must be used to suppress polymerization.



1,3-butadiene sulfone <sup>41</sup> and substituted 1,3-butadiene sulfones <sup>42</sup> have been prepared. The cyclic butadiene sulfone has been used as the monomer in the preparation of poly (butadiene sulfone), but polymerization was found to occur via the decomposition of the cyclic sulfone to butadiene and sulfur dioxide followed by radical copolymerization, rather than by ring opening polymerization. <sup>41</sup>

The copolymerization of sulfur dioxide and alkenes was first reported by Solonina. <sup>43</sup> During the 1930s interest developed in these copolymers since they are formed from readily available, inexpensive raw materials by a reaction which proceeds to high yield under mild conditions. Commercial applications of poly (alkylene sulfones) have been limited by their poor thermal and alkali stabilities. Thermal decomposition of these copolymers at relatively low temperature (ca. 70°C) leads to appreciable reduction in molecular weight. At higher temperatures complete breakdown into the monomers occurs. Monomer recovery of 80% in the thermolysis of poly (propylene sulfone) has been reported. <sup>44</sup> A decomposition mechanism consisting of attack of the sulfone group on the  $\beta$ -hydrogen atoms to form olefins and sulfinic acid, which decomposes to sulfur dioxide has been proposed. <sup>45</sup> The hydrocarbon products, consisting mainly of the starting monomer, are formed by hydrogen transfer reactions and radical termination.

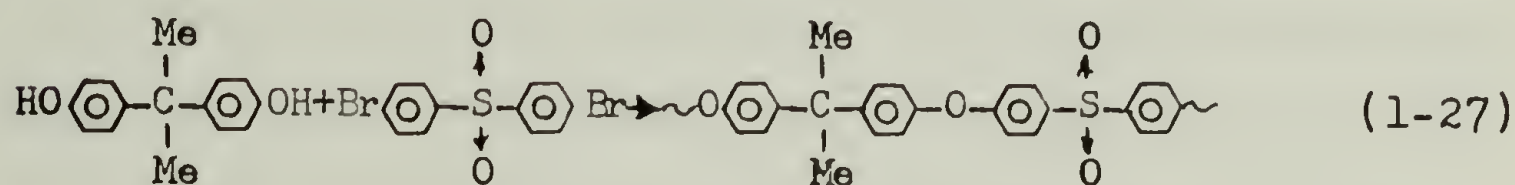


The low level of alkali stability of these copolymers is exemplified by the reduction in inherent viscosity of poly (cis,cis-1,5-cyclooctadiene sulfone) from 1.83 to 0.26 in 1% NaOH at room temperature,<sup>46</sup> and by the reduction in inherent viscosity from 2.39 to 0.12 upon exposure of poly (1,3-cyclo-hexadiene sulfone) to the same environment.<sup>11</sup>

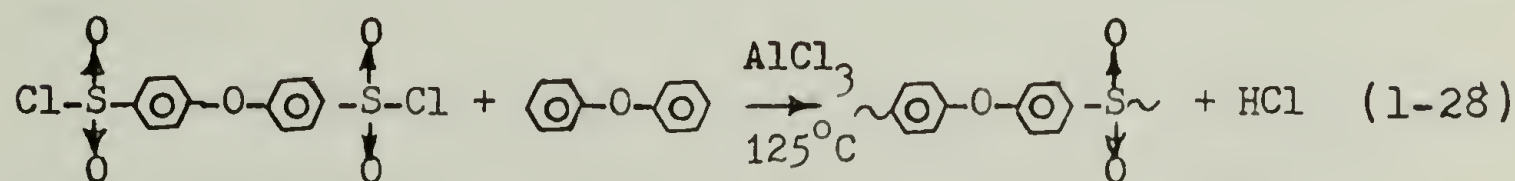
A recent attempt to commercialize a poly (alkylene sulfone) was described by Chatelain.<sup>48</sup> Suspension copolymerization of sulfur dioxide and butene-1 was carried out to produce a polymer bead to which a volatile hydrocarbon (e.g. butane) was added as a blowing agent. Advantages claimed for this foamable copolymer are better solvent resistance, smokeless combustion and lower thermal conductivity than foamed polystyrene.

More recently, interest in polysulfones has been renewed by the commercialization of poly (arylene sulfones) as engineering plastics. These amorphous polymers are completely resistant to aqueous acid, and, due to the stability of the aromatic protons, to alkali. The polymers have excellent thermal stability and, because of the bulk of the

aromatic group and the polar interaction between aromatic and sulfone moieties, show high glass transition temperatures. Poly (arylene sulfones) are prepared by condensation polymerization. A nucleophilic substitution reaction, in which the halide atoms of an activated aromatic dihalide are displaced by phenoxide ions, is the reaction used to produce one of the commercially available aromatic polysulfones, "Polysulfone", manufactured by Union Carbide Corporation.



An electrophilic aromatic substitution reaction, in which hydrogen is displaced as a proton by some form of sulfonylium cation using Friedel Crafts catalysts, is the basis of the second commercial polysulfone, "Polymer 360", manufactured by 3M Company. <sup>49</sup>



Despite the commercial unattractiveness of poly (alkylene sulfones), the addition reaction of sulfur dioxide and alkenes has continued to be the subject of intensive scientific investigation due to interest in the kinetics of a polymerization reaction which proceeds to an



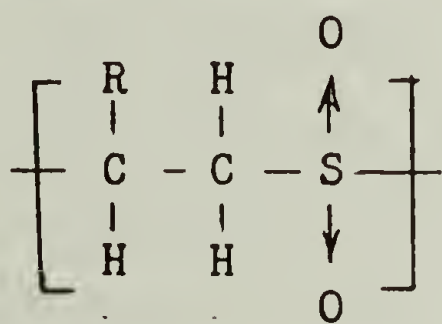
equilibrium at low temperature, and in which the initiation and propagation reactions have been postulated to proceed via a readily identifiable intermediate, a charge-transfer complex. Comprehensive overviews of the literature on this reaction have been given in several review articles. 50,51,52,53

Idl. Copolymer structure. The composition of copolymers prepared by addition of sulfur dioxide to the olefinic double bond is normally equimolar regardless of the ratio of the two comonomers. Exceptions to the equimolar copolymer composition are infrequent and have been attributed to different competing mechanisms. In the formation of poly (1,5-hexadiene sulfone) <sup>54</sup> and poly (cis,cis-1,5-cyclooctadiene sulfone) <sup>55</sup> by cyclocopolymerization of these diallyl compounds, one molecule of sulfur dioxide is incorporated into the chain backbone and another into a ring formed during the polymerization reaction.

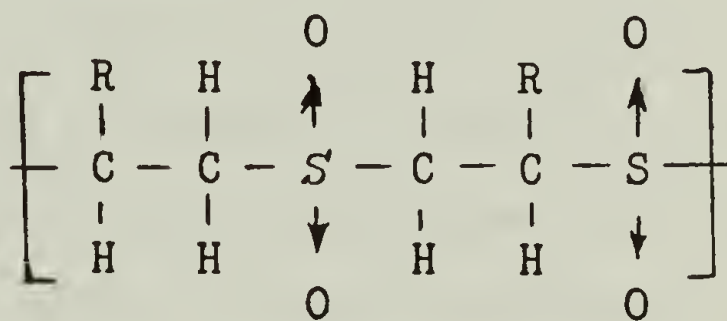
The copolymerization of styrene, <sup>1,10,32</sup> para substituted styrenes <sup>56</sup> and vinyl chloride <sup>57,58</sup> with sulfur dioxide leads to the formation of copolymers containing two molecules of the hydrocarbon monomer to one of sulfur dioxide. Composition variance from the commonly found 1:1 copolymer in the formation of poly (styrene sulfone) has been attributed either to copolymerization

of a 1:1 styrene-sulfur dioxide charge-transfer complex with free styrene,<sup>1</sup> or to the reversibility of the reaction between the growing chain and sulfur dioxide,<sup>59</sup> or to the presence of a bimolecular depropagation reaction.<sup>32</sup>

Poly (olefin sulfones) have been demonstrated to be composed of head-to-tail (1-29) rather than tail-to-tail (1-30) linkages of the hydrocarbon portions by chemical analysis of low molecular weight degradation products or oligomers produced in the presence of chain transfer agents.<sup>51</sup>



(1-29)

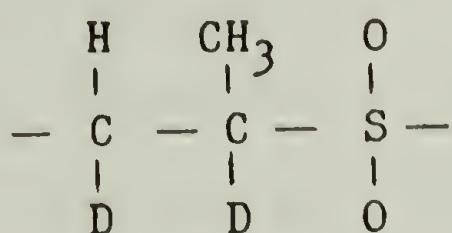


(1-30)

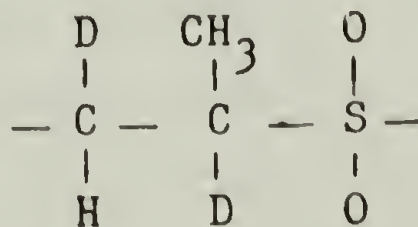
The 100 MHz NMR spectra of poly (propene sulfones) prepared from propene, propene-1,1,3,3,3-d<sub>5</sub>, propene-cis-1,2-d<sub>2</sub>, and propene-2-d<sub>1</sub> were obtained by Ivin and Navratil.<sup>60</sup> Spectra of the polymer prepared from the pentadeuterated monomer, CD<sub>2</sub>=C(CD<sub>3</sub>)H, exhibited a single resonance, indicating that the methyne proton was insensitive to chain tacticity. The methyl resonance of the undeuterated polymer consisted of a single doublet.

indicating that this resonance was insensitive to chain tacticity as well. The main chain proton resonances of the undeuterated polymer consisted of two distinct portions, a downfield part (two protons) and an upfield part (one proton). Since the deuterated polymer containing only methyne protons was shown to have a single resonance in the downfield portion of the spectrum of the undeuterated polymer, the methylene protons of the polymer were shown to be non-equivalent, one having a chemical shift in the upfield part of the main chain proton spectrum, the other having a chemical shift in the downfield portion.

The polysulfone prepared from the dideuterated monomer,  $\text{CHD} = \text{C}(\text{CH}_3)\text{D}$ , exhibited a spectrum in which the relative proportions of a downfield triplet assigned to a cis configuration (1-31) and an upfield doublet assigned to a trans configuration (1-32) in the main chain spectral region depended on the polymerization temperature.



(1-31)



(1-32)

Polymer prepared at  $-80^\circ\text{C}$  possessed an excess of the doublet resonance which was attributed to the trans addition of sulfur dioxide to the double bond leading to the



structure  $\begin{array}{c} \text{D} \text{ CH}_3 \text{ O} \\ \text{C} - \text{C}^3 - \text{S} \\ \text{H} \text{ D} \text{ O} \end{array}$ . The investigators propose a mechanism whereby inversion of the intermediate alkyl radical from trans to cis takes place prior to the addition of sulfur dioxide and increases with increasing temperature. They claim that this system is the first demonstration of a preferred mode of addition in a free-radically initiated polymerization. Assignment of the resonances attributable to the methylene protons in terms of isotactic, syndiotactic and heterotactic triads were made.

Further investigation of the NMR spectra of several straight chain and cyclic olefinic sulfones was performed by Ivin, Navratil and Walker.<sup>61</sup> By analysing spectra in a manner similar to that used in the analysis of poly (propene sulfone) spectra, both main chain and alpha-methylene protons of poly (hexene-1-2-d<sub>1</sub> sulfone) were found to be non-equivalent. Analysis of the spectra of poly (cyclohexene-3,3,6,6-d<sub>4</sub> sulfone) showed the beta protons of this polymer to be non-equivalent. The main chain proton resonances of this polymer showed some variation with preparation temperature which the investigators attribute to tacticity effects which cause the cyclohexane rings to be oriented with respect to the main chain.

The run length of methylene segments between sulfur dioxide moieties in poly (ethylene sulfone) were determined from the analysis of 220 MHz NMR spectra by Ovenall,

Sudel and Cabat.<sup>62</sup> The method was developed by assigning the chemical shifts for the methylene protons based on the model compounds poly (hexamethylene sulfone) and poly (hexamethylene/tetramethylene sulfone). Their analysis indicated that the copolymerization of ethylene and sulfur dioxide appears to proceed by the random copolymerization of an alternating sulfur dioxide-ethylene complex with ethylene.

The microstructures of poly (butadiene sulfone) and poly (butadiene-co-maleic anhydride) were found to be much richer in cis-1,4 structures than those of polybutadiene, poly (butadiene-co-styrene) and poly (butadiene-co-acrylonitrile) copolymers prepared under the same conditions.<sup>63</sup> This result was attributed to stabilization of the cisoid transition state by complex formation occurring through charge-transfer interaction of butadiene with the electron acceptor comonomers in the first two cases. The copolymerization of chloroprene and sulfur dioxide, on the other hand, was found to produce mostly 1,4-trans units,<sup>64</sup> but this copolymer is not strictly an alternating one. The ratio of chloroprene to sulfur dioxide was found to increase with reaction temperature and, at high chloroprene concentration in the comonomer feed, with the initial chloroprene concentration. This effect appears to be due to the concurrent homopolymerization of the weak electron donor,

chloroprene, and the alternating copolymerization of chloroprene and sulfur dioxide.

Id2. Initiation of the copolymerization reaction.

The copolymerization of sulfur dioxide and an unsaturated hydrocarbon is believed to occur by a free radical mechanism. Evidence for this contention is found in the effectiveness of radical producing compounds in initiating the copolymerization. Furthermore, the addition of phenolic compounds which are known to form more stable radicals than the propagating radical has been found to retard the reaction,<sup>65,66</sup> and electron spin resonance spectra indicating the presence of radicals have been reported.<sup>66,67</sup> The alternating structure of the copolymers produced makes it unlikely that an ionic process is occurring because no exactly alternating copolymer made by ionic initiation has yet been reported.<sup>68</sup>

In the copolymerization reaction with alkenes at low temperatures, sulfur dioxide may also act as a solvent for both the comonomer and polymer and as a component of the initiating system as well as being the comonomer itself. In its role as a solvent, its high dielectric constant of 16<sup>69</sup> should be noted since charge separation in ionic processes are facilitated in media of high dielectric constant.



Initiation without interaction with sulfur dioxide.

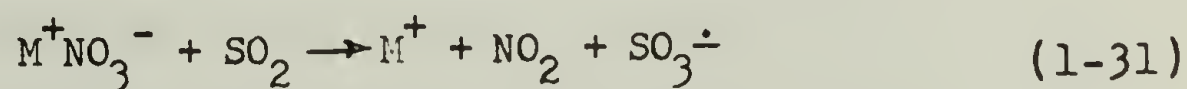
No interaction between initiator and sulfur dioxide was found when peroxides and azo compounds were used. The copolymerization of styrene and sulfur dioxide using azobisisobutyronitrile initiator was found to yield only the 2:1 poly (styrene sulfone). When UV radiation was used to initiate the reaction, the styrene concentration of the copolymer increased when high sulfur dioxide feed concentrations were used.<sup>1</sup> This effect may be attributable to a photolytic reaction involving sulfur dioxide to produce a cationic initiator. Similar polymer molecular weights were obtained in the formation of poly (butene-1 sulfone) initiated by UV radiation or benzoyl peroxide indicating that both initiating processes are monoradical in character.<sup>65</sup> The use of peroxides and azo compounds is limited to temperatures above 25°C. No polymerization was found to occur when lauroyl peroxide or di-t-butyl peroxide were used to initiate styrene-sulfur dioxide copolymerization.<sup>69</sup>

Light of wavelength less than 380 nm has been used to initiate the copolymerization of sulfur dioxide and olefins.<sup>70</sup> Photoactivation of azobisisobutyronitrile by light of 365 nm wavelength was employed to induce the decomposition of the azo compound in the styrene-sulfur dioxide reaction referred to above.<sup>1</sup> The initiating

effect of light radiation in the absence of free radical initiator was found to be 20-40% of the photoactivated catalyzed rate, and may be due to photolysis of the styrene-sulfur dioxide charge-transfer complex.

Initiation of the copolymerization by gamma radiation has been carried out using styrene and vinyl chloride as comonomers with sulfur dioxide.<sup>10,51</sup> As noted in the case of initiation by UV radiation, radiolysis of sulfur dioxide resulted in the participation of a cationic reaction.

Sulfur dioxide interactions with initiators. In contrast to the absence or slight interaction between the above initiators and sulfur dioxide, the most commonly employed and most practical initiators form radicals by a one electron transfer (redox) reaction with sulfur dioxide. As an example, the copolymerizations of 2-butene,<sup>70</sup> cis, trans-1,5-cyclodecadiene<sup>71</sup> and dicyclopentadiene<sup>72</sup> with sulfur dioxide by metal nitrate initiators have been reported. In this case the sulfite radical-ion which is probably formed by the redox reaction of sulfur dioxide and nitrates as follows:



has been suggested as being the initiating species.<sup>73</sup>

Normally, free-radical polymerization is inhibited by molecular oxygen. This inhibition appears to be due to

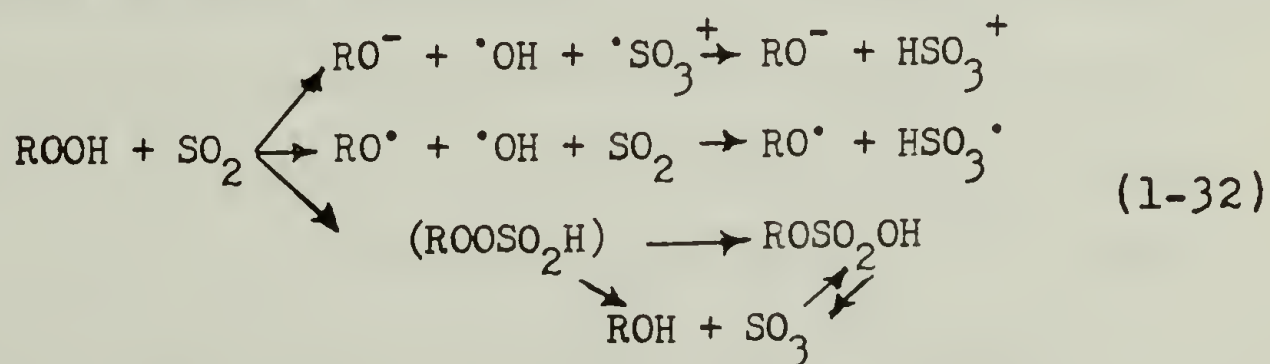
copolymerization of the monomer with oxygen to form unreactive peroxide radicals.<sup>74</sup> In copolymerizations with sulfur dioxide, however, the presence of oxygen has been found to initiate the formation of poly (cyclohexene sulfone) and poly (1,3-cyclohexadiene sulfone).<sup>29</sup>

Oxygen alone or as a "promoter" of a peroxide initiator was used in the preparation of poly (cis,cis-1,5-cyclooctadiene sulfone).<sup>55</sup> The well known reaction of alkenes with molecular oxygen to form hydroperoxides<sup>75</sup> and their subsequent decomposition to free radicals appears to be the cause of this phenomenon. In copolymerization with sulfur dioxide, radical formation is facilitated by electron transfer to sulfur dioxide. This reaction is much faster than the competing copolymerization with oxygen referred to above.

Radical formation by the one-electron transfer, redox reaction between organic hydroperoxides and sulfur dioxide appears to be the simplest effective method of initiating the copolymerization. In their study of the polymerization of styrene in sulfur dioxide, Schulz and Banihaschemi<sup>69</sup> found that polystyrene rather than poly (styrene sulfone) was produced with t-butyl hydroperoxide or perlauric acid initiators at -20°C. No polymerization occurred when either the peroxy compound or the sulfur dioxide was omitted from the recipe. When 1-hexene,



cyclohexene or 2-methyl-1-pentene were used as comonomers, the poly (olefin sulfones) were formed as expected. In solvents of high dielectric constant or in electron donating solvents, polystyrene formation was depressed; either pure poly (styrene sulfone) or a mixture of the two polymers were formed. The formation of polystyrene rather than poly (styrene sulfone) was attributed to cationic initiation of styrene homopolymerization. Initiation by the cationic process was attributed to the production of a sulfuric acid halfester (or its decomposition product, sulfur trioxide) by a reaction between sulfur dioxide and the hydroperoxide. This reaction was assumed to proceed via free radical intermediates. Several possible mechanisms are described by the authors and are reproduced in equations (1-32) :

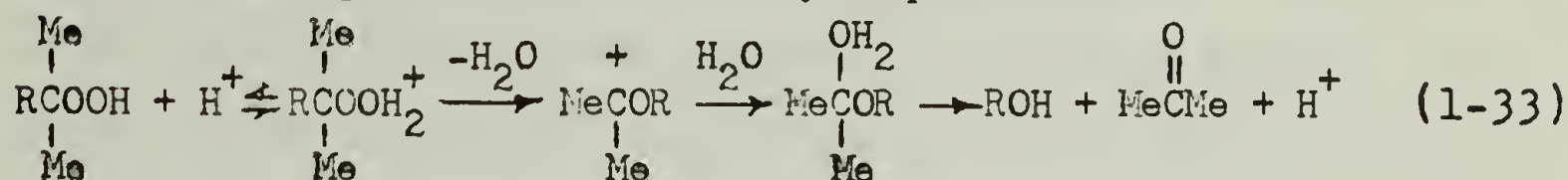


The increased tendency toward cationic polymerization in the styrene-sulfur dioxide system may be attributed to the increased resonance stabilization of the styryl cation compared to olefinic cations. The solvent effect is attributable to the increased counterion separation in media of high dielectric constant and to the competition in

cation formation between monomer and electron donating solvents.<sup>76</sup> The presence of hydroperoxide is not a prerequisite for the cationic polymerization of monomers of high electron donating capacity in sulfur dioxide since the homopolymerizations of vinyl isobutyl ether and  $\alpha$ -methylstyrene have been initiated in sulfur dioxide by ionizing radiation.<sup>10</sup> Trace amounts of sulfur trioxide present in the sulfur dioxide may serve as initiator in these polymerizations. Confirmation of the free radical nature of the initiation mechanism of hydroperoxide initiation of olefin-sulfur dioxide copolymerization was obtained by Eaton and Ivin.<sup>77</sup> They demonstrated that the activation energies of the photochemical and hydroperoxide initiated copolymerizations were identical.

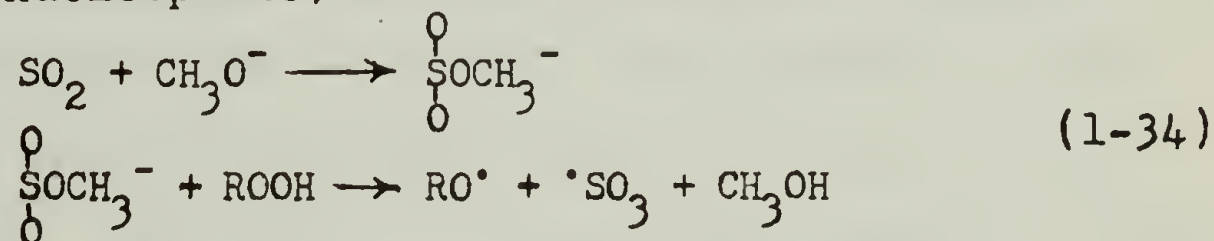
In developing a low temperature initiating system for the polymerization of vinyl chloride, Mazzolini et al. investigated the kinetics of the decomposition of the cumene hydroperoxide-sulfur dioxide system.<sup>78</sup> Their investigation showed that no polymerization occurred in the absence of nucleophilic agents and that the presence of strong nucleophiles (e.g.  $\text{OCH}_3^-$ ,  $\text{OH}^-$ ) led to the formation of poly (vinyl chloride) homopolymer. In the presence of weaker nucleophilic agents (e.g. ethers, ketones) both poly (vinyl chloride) and the polysulfone copolymer were formed. Decomposition of the hydroperoxide with sulfur

dioxide in the absence of nucleophiles yielded phenol and acetone and was attributed to the acid-catalyzed heterolytic decomposition of the hydroperoxide:



This reaction proceeds without radical intermediates. <sup>79</sup>

When a nucleophile was added, a mixture of  $\alpha$ -methylstyrene, acetophenone and cumyl alcohol was obtained. The reaction mechanism in this case was inferred to be the homolytic decomposition of the hydroperoxide, induced by the transfer of an electron from the sulfur dioxide-nucleophile complex. The electron donor (reductant) ability of the sulfur dioxide is enhanced by the addition of a donor group (nucleophile) to the molecule.



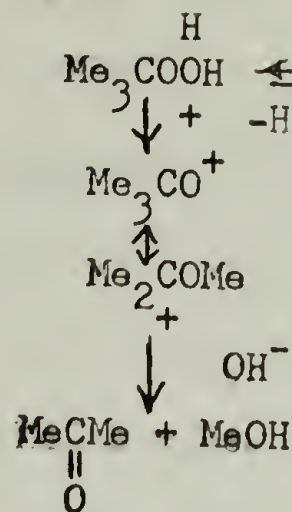
The presence of  $\text{HO}\dot{\text{S}}\text{O}_2$  and  $\text{t-BuO}\dot{\text{S}}\text{O}_2$  radical intermediates in the reaction between t-butyl hydroperoxide and sulfur dioxide in a methanolic medium was confirmed by ESR. <sup>80</sup> The radical half-life was estimated at 90 ms, and a  $10^{-5}$  molar radical concentration was estimated. Radicals were not detectable in weakly nucleophilic solvents (e.g. ether, acetonitrile) confirming the predominance of heterolytic decomposition under these conditions as found by Mazzolini et al. <sup>78</sup> Further ESR studies by these



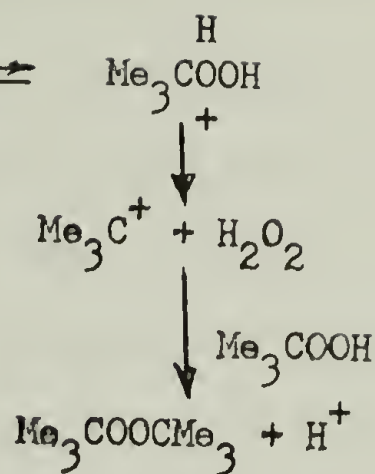
investigators demonstrated the existence of  $\text{RM}^\bullet$  radicals when monomers which do not form equimolar polysulfones (e.g. styrene, vinyl chloride, acrylonitrile) were added to the above initiating system.<sup>81</sup> (R is a radical fragment of the initiator decomposition (e.g.  $\text{HOSO}_2^\bullet$  or  $\text{t-BuOSO}_2^\bullet$ ) and M is a radical fragment derived from the monomer (e.g.  $\text{CH}_2^\bullet\text{CHPh}$ .) The ESR spectra of the initiating system with 1-hexene and allyl alcohol indicated that  $\text{RMSO}_2^\bullet$  radicals were formed by the addition of these alkenes which form equimolar polysulfones.

In a study aimed at clarifying the mechanism of the effectiveness of sulfur compounds as antioxidant synergists, Chien and Boss investigated the reaction of t-butyl hydroperoxide and sulfur dioxide.<sup>82</sup> In the presence of 2,6-di-t-butyl-p-cresol to inhibit decomposition to free radicals, the reaction proceeded rapidly to form an immiscible layer. Analysis of the products revealed that the sulfur dioxide was quantitatively converted to sulfuric acid. Ditertiary butyl peroxide was found to be the only other reaction product at  $-60^\circ\text{C}$ , while at  $25^\circ\text{C}$  a small amount of acetone was formed as well. The reaction mechanism was presented as consisting of electrophilic addition to the hydroperoxide to form an oxonium ion followed predominantly by C-O bond cleavage (1-36), with a minor amount of O-O bond cleavage (1-35) occurring at the higher

temperature.



(1-35)



(1-36)

Cumene hydroperoxide was used as the initiator in the preparation of poly (chloroprene sulfone).<sup>83</sup> Both the overall rate of polymerization and the sulfur content of the resulting copolymer were found to increase with increasing sulfur dioxide concentration of the feed mixture. All of the copolymers produced were less than equimolar in sulfur dioxide to chloroprene content. Reaction yields at relatively high initiator concentrations (e.g. 1.3% of chloroprene) increased to a constant value not exceeding 5% at 20°C. The apparent activation energy of the overall polymerization reaction was found to be negative. The addition of ether inhibited polymerization while p-benzoquinone did not affect the initial polymerization rate. Based on the increased reaction rate at low temperature and the inhibiting effects of ether and p-benzoquinone these investigators concluded that both free radical and cationic polymerizations were taking place. This was apparently borne out by the variable copolymer composition which

resulted from the free radical alternating copolymerization in conjunction with the cationic homopolymerization.

Spontaneous initiation. The most interesting observations relative to initiation in the copolymerization of sulfur dioxide and alkenes are instances of "spontaneous" initiation (i.e. polymerization without initiator) reported to occur in reactions with strained ring cyclic olefins. Zutty et al. found that initiation of the copolymerization of norbornene (bicyclo (2.2.1) hept-2-ene) and sulfur dioxide appeared to proceed spontaneously and very rapidly at  $-20^{\circ}\text{C}$ .<sup>66</sup> From this observation and the fact that the molecular weight of the polymer was shown to increase with time at constant conversion, it was concluded that the initiating entity was a biradical formed by the rearrangement of the charge-transfer complex of norbornene and sulfur dioxide. Propagation of the polymerization was postulated to occur through biradical coupling involving long-lived free radicals. Disproportionation of the biradical would regenerate monomers which would repolymerize spontaneously. The investigators stated that repeated purification by distillation of the norbornene increased the tendency of the monomers to polymerize spontaneously. Removal of residual peroxides prior to final distillation by extraction with ferrous sulfate or distillation from sodium was stated not to affect the activity of the norbornene.



A prior reference to the preparation of poly (norbornene sulfone) stated that an initiator, t-butyl hydroperoxide, was required.<sup>84</sup> In contrast to the results of Zutty, Sartori and Lundberg were unable to observe spontaneous polymerization in the norbornene-sulfur dioxide system.<sup>85</sup> Their results point to the adventitious formation of hydroperoxides in the norbornene or solvent by oxidation with air during storage as the cause of reported instances of spontaneous initiation. Additional evidence against the occurrence of spontaneous initiation was provided by Vanhearen and Butler.<sup>86</sup> In conducting studies of the copolymerization of norbornadiene (bicyclo (2.2.1)2,5-heptadiene) with sulfur dioxide, they found that, while an apparent spontaneous initiation occurred in dioxane or cyclohexanone, the phenomenon was not observed if these solvents were freshly distilled under nitrogen immediately prior to use, or in undistilled solvents in which oxidation to hydroperoxide is unlikely (e.g. toluene, n-heptane, acetonitrile).

Other investigators reported the occurrence of apparent spontaneous copolymerization of sulfur dioxide with cycloolefins. The formation of poly (1,3-cyclohexadiene sulfone) without initiators at temperatures as low as -78°C has been discussed.<sup>47</sup> Yamashita and coworkers describe the spontaneous copolymerization of sulfur dioxide

with 1-methylcyclopropene<sup>67</sup> and cyclopentene.<sup>87</sup> The observations that no initiator was required and that the rate of polymerization depended on the second power of the initial sulfur dioxide concentration and on the third power of the olefin concentration led the investigators to conclude that a charge-transfer complex participated in both the initiation and propagation steps. Yamashita et al. emphasized the role of ring strain in the cycloolefin in increasing the tendency toward spontaneous initiation. They pointed out that spontaneous initiation occurs in copolymerization of cyclopentene while neither cyclohexene nor cyclooctene copolymerized spontaneously with sulfur dioxide. This analogy appears to be overdrawn since the ring strain energy of cyclopentene, 1.3 kcal/mole, although higher than the energy of the unstrained cyclohexene ring, is approximately equal to that of cyclooctene, 1.2 kcal/mole.<sup>88</sup> In another article Yamashita et al. compared the polymerizability of donor-acceptor pairs with the donor-acceptor equilibrium constant,  $K_c$ .<sup>89</sup> Complexes of limited stability, (i.e.,  $K_c$  approximately equal to 0.001 l/mole) were claimed to form alternating copolymers upon the addition of free-radical initiators. When the complex equilibrium constant increased to 0.01, spontaneous alternating polymerization was said to occur. Complexes of approximately

unity equilibrium constant were claimed to initiate the cationic homopolymerization of the strongly electron donating donor monomer, while complexes of equilibrium constant greater than 5 were stated to be too stable to enter into polymerization reactions. In the light of the slight difference in equilibrium constant between the sulfur dioxide charge-transfer complexes of cyclopentene, 0.038 at 20°C, and cyclohexene, 0.055 at 20°C, <sup>34</sup> the spontaneity of sulfur dioxide-cyclopentene copolymerization does not appear to be explicable by the above classification scheme.

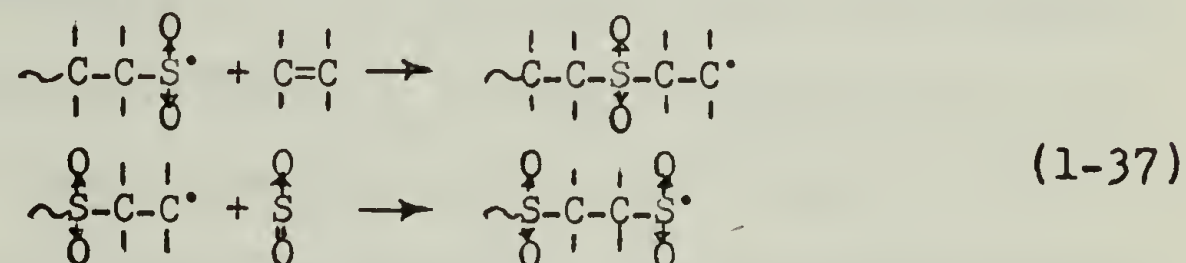
In view of the remark <sup>87</sup> that the surface of the precipitated poly (cyclopentene sulfone) was colored, the possibility of adventitious inclusion of an oxidizing agent (e.g. hydroperoxide) which serves as the actual polymerization initiator cannot be ruled out. Snow and Frey <sup>70</sup> found that polysulfones formed by initiation with ozonized olefins, hydrogen peroxide or other strong oxidizing materials were colored, and that traces of sulfuric acid and hydrocarbon polymers had been found in resins polymerized in reactions in which these initiators were used.

Id3. Propagation reaction. Two phenomena which occur infrequently in addition polymerization reactions are commonly observed in the copolymerization of sulfur

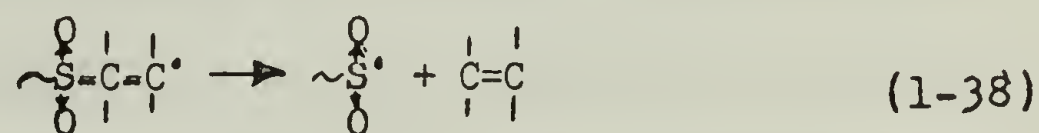


dioxide and alkenes. A ceiling temperature exists, (i.e. no polymerization occurs above a certain temperature) and as discussed previously, alternating copolymers are formed. Both of these observations relate to the propagation reaction.

Ceiling temperature. The ceiling temperature phenomenon is brought about by competition between two reactions occurring during propagation of the radical chain. Formation of the radical chain is due to the addition of free radicals to the unsaturated double bond. This may be represented by reactions (1-37) in which chain propagation in the alternating copolymerization is assumed to proceed via alternating addition of the comonomers:



A chain depropagation reaction assumes greater importance at higher temperature. This reaction is illustrated in polysulfone formation by a beta-scission elimination reaction of the alkyl radical:



The ceiling temperature is a well defined temperature above which the formation of long chain polymer will not occur.<sup>90,91</sup> At the ceiling temperature the rate of forward reaction equals the rate of reverse reaction and the reaction is in thermodynamic equilibrium. The ceiling temperature,  $T_c$ , is thus defined by the thermodynamic relation:  $T_c = \Delta H_p / \Delta S_p$ , where  $\Delta H_p$  and  $\Delta S_p$  are the enthalpy and entropy changes of the polymerization reaction under the experimental conditions when the free energy change of the reaction equals zero. A ceiling temperature is found only in exothermic aggregation reactions and is analogous to physical exothermic aggregation processes, such as freezing, when the aggregation process of freezing is in equilibrium with the disaggregation process of melting. In most polymerization reactions the ceiling temperature is too high to be detectable; in polysulfone formation the ceiling temperature is often near room temperature. This phenomenon was, in fact, first observed in the copolymerization of sulfur dioxide and olefins.<sup>70</sup>

An expression relating the monomer concentration at equilibrium to temperature may be derived by equating the rate of polymerization,  $k_p[M][R\cdot]$ , to the rate of depolymerization,  $k_R[R\cdot]$ , where  $k_p$  and  $k_R$  are the rate constants of propagation and depropagation respectively,  $[M]$

is the monomer concentration (assumed equal to the activity of the monomer) and  $[R]$  is the concentration of active centers, and substituting the Arrhenius expressions for the rate constants:

$$T_c = -\Delta H_p / R \ln(A_p [M]_e / A_r) = \Delta H_p / (\Delta S_p^\circ + R \ln [M]_e) \quad (1-39)$$

In this equation  $R$  is the gas constant,  $A_p$  and  $A_r$  are the frequency factors for the polymerization and depolymerization reactions,  $[M]_e$  is the monomer concentration at equilibrium,  $-\Delta H_p$  is the heat of polymerization, i.e., the activation energy of the propagation reaction minus that of the depropagation reaction, and  $\Delta S_p^\circ$  is the standard entropy change of the polymerization reaction. Equilibrium monomer concentrations at 25°C range from  $10^{-9}$  mole/l for monomers with very slight depropagation tendency (e.g. vinyl acetate) to 310 mole/l for the isobutene-sulfur dioxide system. 92

In the alternating copolymerization of sulfur dioxide and alkenes the overall polymerization reaction may be written:  $DS_n + D + S \rightarrow DS_{n+1}$ , where  $D$  denotes the donor alkene,  $S$  the sulfur dioxide, and  $DS_n$  and  $DS_{n+1}$  are the growing chains of length  $n$  and  $n+1$ . In this case the product of the comonomer concentrations at equilibrium,  $[S]_e [D]_e$  may be substituted for the equilibrium monomer concentration,  $[M]_e$ , to arrive at the expression:



$$T_c = \Delta H_p / (\Delta S_p^0 + R \ln[S]_e [D]_e) \quad (1-40)$$

for the ceiling temperature of alternating copolymerization in terms of the concentrations of the individual monomers. The above equation is applicable to either propagation by alternate comonomer addition or charge-transfer complex propagation, in which case  $[S]_e [D]_e$  is proportional to the charge-transfer complex concentration at equilibrium.

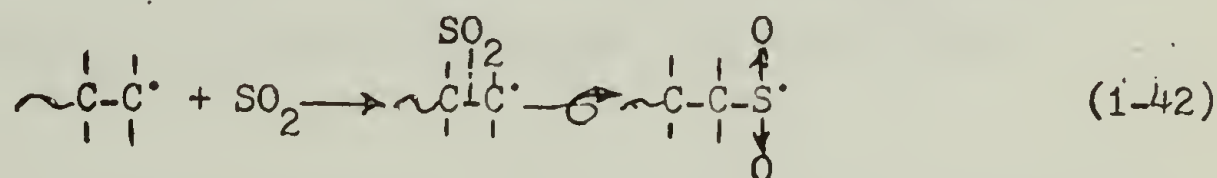
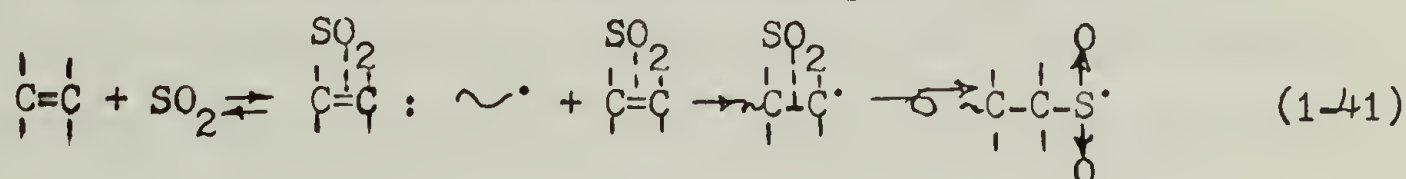
The effect of olefin structure on the ceiling temperature in the formation of polysulfones was investigated by Cook et al. <sup>92,39</sup> They found that branching invariably lowered the ceiling temperature and that the effect was greatest when the branch was at the double bond. An electronegative substituent was found to produce a lower ceiling temperature than an alkyl substituent. The standard entropy change in polymerization was found to lie within the limits of  $60 \pm 3$  e.u. for all of the alkenes tested. The increased depolymerization tendency of branched monomers was attributed to increasing restriction to rotation of the resulting polymer chain due to steric hindrance between the sulfonyl oxygen and substituents on the olefin. This effect, in turn, was associated with a decreased heat of polymerization in going to the more sterically hindered polymer molecule,

although the possibility of increased entropy change in the reaction of branched monomers was not ruled out.

For binary mixtures of alkenes and sulfur dioxide, the ceiling temperature goes to a maximum as the mole fraction of alkene increases from zero to unity. The equation relating ceiling temperature to comonomer concentration for alternating copolymerization predicts that the maximum ceiling temperature should occur at equimolar comonomer concentration (assuming that concentrations and activities are equal). Brady and O'Donnell found that the expected maximum in the ceiling temperature-concentration curve for polysulfone formation did not occur at a mol fraction of 0.5.<sup>94</sup> They attributed this phenomenon to the fact that the thermodynamic states of the insoluble polymers which are formed in sulfur dioxide rich and olefin rich media are not the same. These investigators demonstrated that the polymer precipitated in an amorphous state from olefin rich mixtures while the polymer, swollen by sulfur dioxide, precipitated in a crystalline state from sulfur dioxide rich media.

Alternating copolymer formation. The formation of a polymer chain consisting of exactly alternating sequences of electron donor and electron acceptor units may be explained either by (1) a very high selectivity of a given radical for the opposite monomer based on the

relative rates of competing radical monomer addition reactions; or by (2) the prior reaction of the comonomers to yield an equimolar complex followed by homopolymerization of this complex, (1-41); or by (3) formation of a complex at the end of the propagating chain consisting of an electron donating (or accepting) radical and an electron accepting (or donating) monomer, (1-42). In either of these latter two reaction paths, stabilization of the intermediate states occurs by electron transfer or electrostatic attraction between an electron donor (monomer or radical) and an electron acceptor as follows:



Although intensive investigations have been undertaken to clarify the mechanism, no clear evidence exists to distinguish between the various possible routes. Some of the methods which have been used to clarify the cause of the alternating structure of polysulfones are described below.

Existence of charge-transfer complex. Barb showed the existence of the charge-transfer complex in the styrene-sulfur dioxide system through its optical absorption at 365 nm.<sup>1</sup> Spectrophotometric evidence that this complex

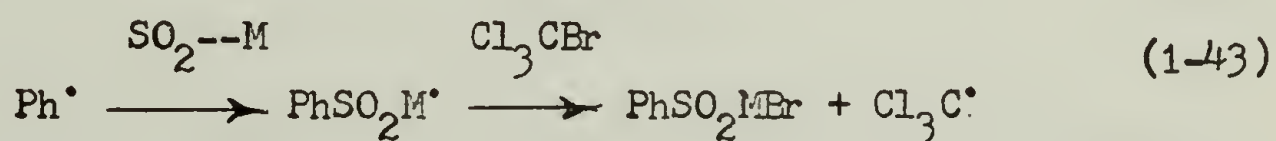


was an equimolar one was provided by Matsuda et al. using the method of continuous variation.<sup>32</sup> Due to its 2:1 alternating polymer structure, the styrene-sulfur dioxide system is considered in further detail below. The charge-transfer complex equilibrium constants, heats and entropies of formation and the extinction coefficients of olefin-sulfur dioxide mixtures were determined optically by Booth et al.<sup>34</sup> Alternating polysulfones prepared from several of these olefins including cyclopentene,<sup>87</sup> cis and trans-2-butene,<sup>95</sup> isobutene<sup>96</sup> and cyclohexene<sup>61</sup> have been reported. There appears to be no doubt that charge-transfer complex formation accompanies polysulfone polymerization, but whether or not the two reactions are interconnected has remained an open question.

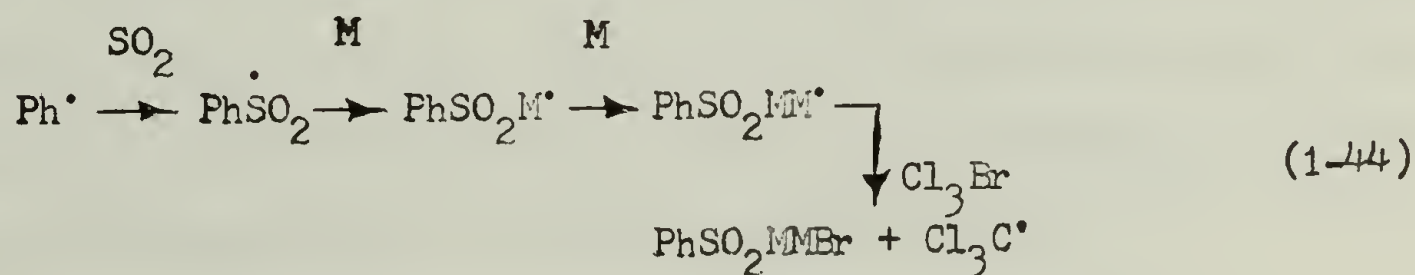
Polymer stereochemistry. The formation of predominantly cis-poly (butadiene sulfone)<sup>63</sup> and of predominantly trans-poly (chloroprene sulfone)<sup>64</sup> has been attributed in the former instance as evidence of propagation via the charge-transfer complex, and in the latter as proof of the non-participation of the complex in the formation of this non-alternating copolymer. This evidence does not, in fact, prove participation of a complex which is formed prior to propagation (mechanism (1-41)) since stabilization of the cisoid transition state

(mechanism (1-42)) may occur at the end of the growing chain by electronic or electrostatic interaction with the entering monomer.

Oligomerization study. The monomeric addition product and oligomers of the reaction of octene-1 and sulfur dioxide were obtained by initiating the oligomerization with benzoyl peroxide in the presence of a good chain transfer agent, bromtrichloromethane.<sup>97</sup> Tokura et al. reported that  $\pi$ -type radicals would not attack sulfur dioxide.<sup>98</sup> whereas phenyl radicals readily add to this comonomer.<sup>99</sup> Based on Tokura's observations and the structure of the resulting oligomeric addition products it was inferred that the products were formed by the concerted addition of both comonomers as a unit (equation (1-43)):



No oligomer with two successive alkyl units, which could be formed by addition of a sulfonyl radical to an olefinic  $\pi$ -type double bond, was found:



Since other polysulfones, notably poly (styrene sulfone), have structures consisting of two successive alkyl residues, this evidence neither confirms nor negates the participation of a complex in the reaction but may simply be an indication of the relatively low reactivity of alkenes to radical addition reactions compared to styrene.

Kinetic studies. In investigations of the spontaneous copolymerization of cyclopentene<sup>87</sup> and 1-methyl cyclopropene<sup>67</sup> with sulfur dioxide the concept of propagation via the charge-transfer complex was advanced by Iwatsuki, Kokubo and Yamashita. Major evidence for assumption of a charge-transfer mechanism was the high order in sulfur dioxide and alkene concentration of the empirically-determined kinetic equation:

$$R_p = k[S]_0^2[D]_0^3 \quad (1-45)$$

where  $R_p$  is the observed initial polymerization rate and  $[S]_0$  and  $[D]_0$  are the initial concentrations of sulfur dioxide and alkene, respectively. The conclusion of these investigators as to the participation of the charge-transfer complex in the "spontaneous" initiation has been examined in section Id2 and should be reexamined in light of the investigation of Sartori and Lundberg.<sup>85</sup>

Since the propagation mechanism advanced by Iwatsuki et al. is based on the participation of the



complex in the initiation reaction, the fit of their experimental data to this mechanism cannot be taken for proof of the participation of the complex in the propagation reaction. Iwatsuki et al. further found that the rate of cyclopentene copolymerization increased to a maximum when the ratio of alkene to sulfur dioxide in the monomer mixture was approximately unity. This observation appears to indicate that a 1:1 complex participates in the reaction since the equimolar complex concentration is a maximum when the components are present in equimolar proportion. The empirical kinetic equation which Iwatsuki et al. derived from their data also shows that a maximum rate should occur at a sulfur dioxide mole fraction of 0.4. It should be noted that in an alternate kinetic model based on propagation by alternating addition of the comonomers and first order initiation due to the adventitious inclusion of peroxides in the alkene, a maximum reaction rate is also obtained as a function of initial comonomer concentration and is related only to rate constants. This alternate reaction mechanism leads to the equation:

$$R_p = c(k_s [S]_o [D]_o^n + k_c [D]_o^{n+1}) \quad (1-46)$$

where  $n$  is the order of the termination reaction,  $c$  is proportional to the initiator decomposition and termination rate constants, and  $k_s$  and  $k_c$  are the propagation rate constants of the addition of sulfur dioxide and alkene, respectively. Equating  $dR_p/d[D]_0$  to zero leads to a definition of the alkene concentration at which a maximum rate occurs,  $[D]_{0max}$ , in terms of the rate constants of the propagation reaction:

$$[D]_{0max} = nk_s / ((1+n)(k_c - k_s)) \quad (1-47)$$

If the maximum occurs at equimolar concentration of the two components, the ratio  $k_c/k_s$  equals 1.67 if bimolecular termination is assumed, and 1.0 in the case of monomolecular termination.

In summarizing the kinetic interpretation of the role of the charge-transfer complex obtained in his comprehensive studies of the formation of poly (olefin sulfones) <sup>65,95,100</sup> and those of others, Ivin stated that experimentation to distinguish between propagation by the addition of complexes and propagation by addition of the separate monomers is difficult to devise. <sup>51</sup> He further noted that claims regarding the interpretation of kinetic or copolymer composition data as being indicative of the participation of the complex do not necessarily prove that this mechanism is correct.

Copolymer composition. The styrene-sulfur dioxide system has been studied extensively in order to clarify the role of the charge-transfer complex in polysulfone formation. In common with poly (vinyl chloride sulfone), polymer sequences of two hydrocarbon segments followed by one sulfone group are usually formed in the copolymerization of styrene and sulfur dioxide. By studying the variation of copolymer composition with dilution and temperature, conclusions relative to the role of the complex should be more easily obtainable.

Poly (styrene sulfone) prepared at room temperature has been shown by elemental analysis to consist of two styrene and one sulfone moieties for feed compositions between 15 and 90% sulfur dioxide.<sup>1,10,32</sup> At higher (due to the aforementioned cationic homopolymerization) and lower sulfur dioxide concentrations the copolymer appeared enriched in styrene units. With decreasing reaction temperature, the styrene concentration of the copolymer decreased, becoming approximately equimolar at  $-78^{\circ}\text{C}$ .<sup>10</sup> The copolymer composition was shown to become less rich in styrene units as the total monomer concentration, styrene plus sulfur dioxide, was decreased.<sup>32</sup> These results have been interpreted in terms of propagation via a charge-transfer complex as well as propagation by alternate addition of the comonomers. Both



interpretations lead to the same kinetic expressions. <sup>54</sup> An additional effect due to ionic homopolymerization has been invoked to account for the increased styrene content of copolymers prepared at high sulfur dioxide concentration and/or low temperature.

Barb interpreted copolymerization results at 20°C and higher temperatures as the radical copolymerization of an equimolar charge-transfer complex and free styrene with the following reaction steps:

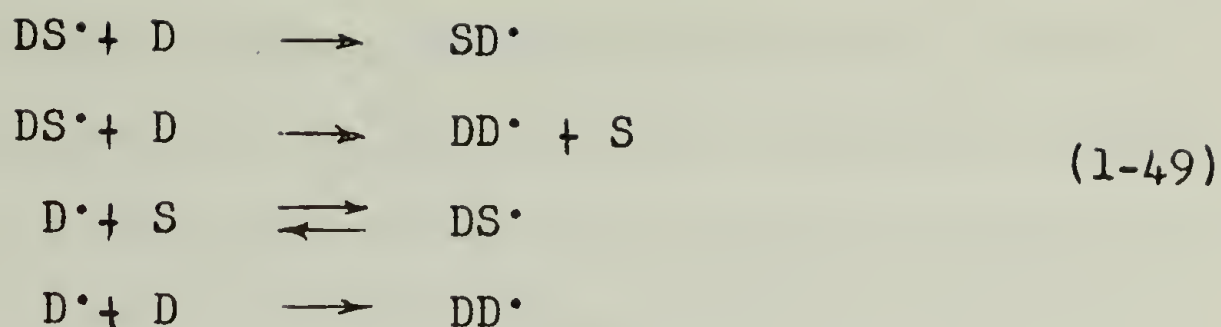


where D represents the styrene monomer and C the equimolar styrene-sulfur dioxide complex. <sup>1</sup> Since the ratio of styrene to sulfur dioxide in the copolymer was always found to equal or exceed 2:1, addition of the complex radical to the complex (the last reaction listed) was excluded. The copolymer composition results obtained by Barb were interpreted by Walling as being equally consistent with a mechanism in which penultimate addition and reversibility effects took part in the polymerization. <sup>54</sup>

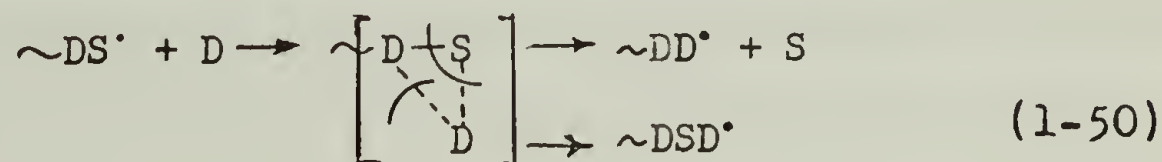


In this reaction scheme  $D'$  is a DSD unit. Addition to sulfur dioxide (second reaction listed) was assumed to be rapidly reversible at all temperatures, while the addition to styrene (third reaction) was postulated to become reversible only at high temperature.

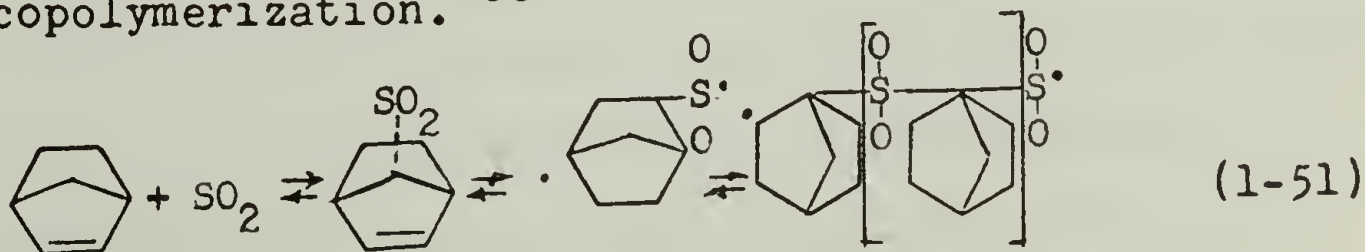
Matsuda et al. found that the copolymer composition varied with total comonomer concentration for polymerizations conducted at 50°C as would be expected if a complex took part in the propagation reaction.<sup>32</sup> The concentration of the complex, at constant total comonomer concentration, is maximum at equimolar comonomer ratio. Thus, a change in the copolymer composition should be observed as the feed composition is changed. Since no variation in copolymer composition was observed between 15 and 90% sulfur dioxide feed concentration, and since the above mentioned change in copolymer composition did not occur when the polymerization was conducted at 0°C, these authors claimed that the complex does not participate in the propagation reaction. These investigators proposed a tentative mechanism involving a second order depropagation:



where the first order depropagation reaction (reverse of third reaction) and the homopropagation reactions are unimportant at low temperatures. The concept of the second order depropagation reaction was illustrated by assuming an intermediate with two possibilities of bond cleavage depending on the reaction temperature.



Biradical propagation. Based on the observations that the molecular weight of poly (norbornene sulfone) produced under certain conditions increased at essentially constant conversion, that very high molecular weight polymer was produced very rapidly and that a high free radical concentration was detected by ESR, Zutty et al. proposed a biradical propagation mechanism for this copolymerization. <sup>66</sup>



Some aspects of this "living" free radical mechanism were discussed in section Id2 in relation to the initiation reaction.



Sartori and Lundberg determined that the molecular weight distributions,  $\bar{M}_w/\bar{M}_n$ , of these copolymers ranged from 2.5 to 4 rather than the fairly narrow distributions which might be expected of living polymers (analogous to those prepared by an anionic mechanism) or to the most probable distribution ( $\bar{M}_w/\bar{M}_n = 2$ ) which would result from simple condensation of radicals.<sup>85</sup> They attributed the high radical concentration observed by Zutty et al. to the very rapid decomposition of adventitious traces of hydroperoxides induced by the presence of sulfur dioxide. These investigators found that molecular weight did indeed increase with conversion but could not duplicate the increase in molecular weight with time at constant conversion. Sartori and Lundberg attributed the molecular weight increase with increasing conversion to hindered termination due to the high viscosity of the medium at high conversion. They further pointed out the analytical difficulties in obtaining reliable molecular weight data in view of the rapidity of the reaction.

Id4. Termination reaction. Termination of the radical chain may be expected to occur chiefly by the collision of two of the growing chains. Termination of the radical activity may be caused by pairing of the free electrons, i.e., combination, or by the transfer of a proton beta to the carbon atom carrying a free electron in

the colliding radical, i.e., disproportionation. Since both alkyl and sulfonyl radicals are present, three mutual termination reactions are possible including termination of like radicals with each other and cross-termination of unlike radicals. Additionally, radical transfer reactions may occur which lead to the formation of stable radicals (degradative chain transfer) or a radical may become inactive due to isomerization or due to its being physically trapped in solid polymer which does not permit diffusion of monomer to the radical site.

Very little is known concerning the chemistry or the exact mechanism of the termination reaction in polysulfone formation. Barb determined the termination rate constant in the copolymerization of styrene and sulfur dioxide.<sup>1</sup> Postulating that propagation proceeds via the complex and that the complexyl radical has the structure  $\text{SO}_2\text{M}\cdot$  (and assuming that combination of  $\text{M}\dot{\text{S}}\text{O}_2$  radicals, although subsequently found to occur, would be sterically and electrostatically unlikely), he showed that the three termination rate constants would be equal. He determined the absolute value of the propagation rate constant from rotating sector experiments and  $k_p^2/k_t$  from experiments relating the rate of decrease of the sulfur dioxide concentration to time and a model based on the above assumptions. The value of  $k_t$  at 20°C,  $10^7 \text{ l mol}^{-1}\text{sec}^{-1}$ ,

was found to be of the order of magnitude expected for D-D termination as determined for styryl radicals.

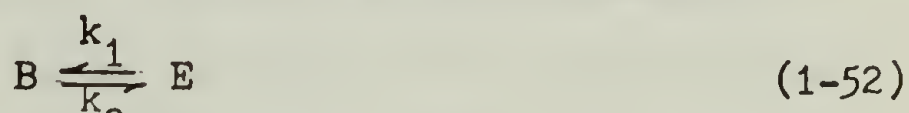
Barb's assumption of the structure of the terminal group was confirmed by the ESR spectra of Flockhart et al. who assigned the spectrum of the propagating radical in this copolymerization to the structure  $R(SO_2)CH_2\dot{C}H$ , where R is OH or t-Buo, fragments of the t-Butylhydroperoxide initiator used.<sup>80</sup>

Interpretation of the kinetics of poly (olefin sulfone) formation indicated cross-termination to be controlling when butene-2 was the olefin but that S-S termination controlled the copolymerization of 1-hexadecene with sulfur dioxide.<sup>100</sup> Exponents of the initiator concentration in the relationship between initiator concentration and polymerization rate have generally been found to range between 0.5 and 0.8.<sup>51</sup> This suggests that, although termination is principally via a biradical mechanism, some linear termination (i.e., degradative chain transfer) occurs as well.

Id5. Negative apparent activation energy. In several of the kinetic investigations of the polysulfone reaction, a negative temperature coefficient of the reaction rate or a maximum in the reaction rate-vs.-temperature relationship was found to exist. This phenomenon can occur when the measured rate is controlled by two or more elementary



reactions with different temperature coefficients. If it is assumed that the activation energy does not vary appreciably with temperature, anti-Arrhenius behavior can lead to an increasing reaction rate with decreasing temperature only if the rate equals the difference of two or more terms each consisting of a rate constant (with exponential temperature dependence) and a concentration. This occurs when the reverse reaction enters into the kinetic expression, i.e., when one of the reaction steps approaches an equilibrium. Using the simple example:



$$\frac{d B}{d t} = -\frac{d E}{d t} = A_1 [E] \exp \frac{\Delta H_1^\ddagger}{R T} - A_2 [E] \exp \frac{\Delta H_2^\ddagger}{R T} = k_1 ([B] - \frac{[E]}{K}) \quad (1-53)$$

The temperature coefficient of the equilibrium constant,  $K$ , is given by the van't Hoff equation:

$$\frac{d \ln K}{d T} = \frac{d \ln k_1}{d T} - \frac{d \ln k_2}{d T} = \frac{\Delta H}{R T^2} \quad (1-54)$$

A negative temperature coefficient of the reaction rate can only occur when the equilibrium constant decreases with increasing temperature, i.e., when the reaction is exothermic. It can readily be shown that neither competing reactions nor consecutive reactions without an exothermic equilibrium can lead to increasing reaction rate with decreasing temperature.

Hrabak et al. found that conversion in the reaction of chloroprene and sulfur dioxide increased very rapidly

in the first ten minutes of the reaction, then appeared to increase only slightly thereafter.<sup>83</sup> A decrease in temperature increased the initial rapid rate and decreased the subsequent slow rate slightly. Based on the inhibiting effect of ether on the initial rate and that of benzoquinone on the subsequent slow rate they attributed the negative temperature coefficient of the initial rate to a cationic polymerization mechanism.

A maximum in the initial rate-vs.-temperature relationship was found to exist in the copolymerization of 1,3-cyclohexadiene and sulfur dioxide.<sup>47</sup> The investigators assumed that this effect was related to a change in miscibility of the components in the medium which correlated with the temperature effect on rate.

Schneider et al. determined that the sulfur dioxide/vinyl chloride ratio increased with decreasing temperature in the copolymerization of these two monomers.<sup>57</sup> Their investigation revealed that the reaction rate increased with decreasing temperature at low concentrations of vinyl chloride in the feed, went through a maximum with decreasing temperature at intermediate feed comonomers ratio, and decreased with decreasing temperature at low concentrations of sulfur dioxide in the feed. They further showed that the maximum reaction rate was found at low temperature and at a comonomers feed



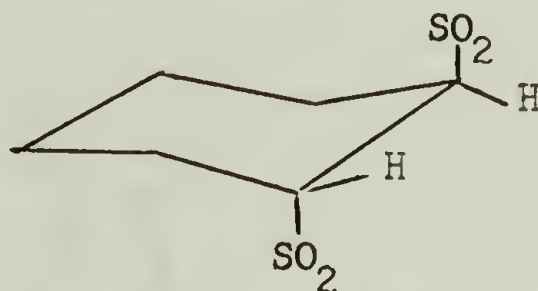
composition equal to the stoichiometric composition of a complex as determined from a freezing point diagram.

These investigators attribute the anomalous temperature behavior to the increasing participation at low temperature of a complex whose concentration increases as temperature is decreased.

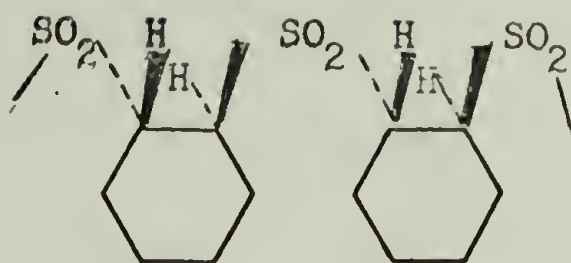
Id6. Copolymerization of cyclohexene and sulfur dioxide. Although this system appears to have been investigated in the past, very little information concerning the kinetics of polysulfone formation or product characterization appears in the literatures. Seyer and King initiated the copolymerization of the two monomers by bubbling air through moist cyclohexene to form a white, amorphous compound, soluble in chloroform, which decomposed at about 250°C with the liberation of sulfur dioxide.<sup>29</sup> Frederick et al. used hydrogen peroxide to initiate the copolymerization.<sup>102</sup> They obtained a white, amorphous solid which softened and decomposed slightly at 200°C. The polymer had a number average molecular weight of 5700 and contained hydroxyl end groups. Ascaridole, a transannular peroxide, was found to be an effective initiator of the copolymerization.<sup>103</sup> Gamma ray initiated copolymerizations were conducted by Henglein et al. who obtained a light brown compound of 2200 molecular weight.<sup>104</sup>



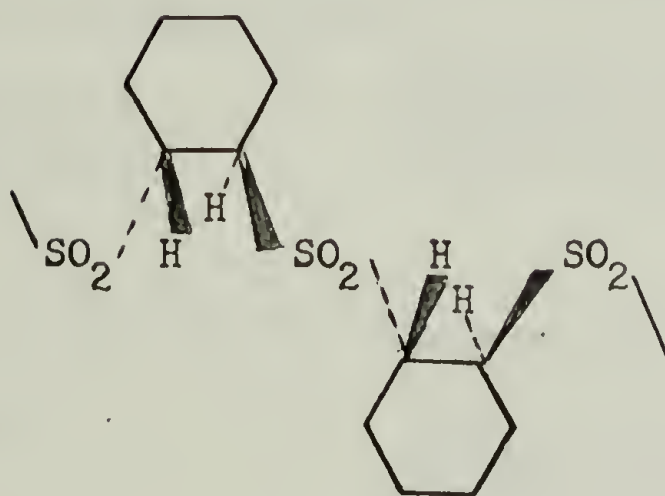
The ceiling temperature of the reaction was found to be 24°C and the heat of polymerization was estimated to be -17.8 kcal/mole based on the ceiling temperature and an approximate value of the entropy change during the reaction, -66.55 e.u..<sup>93</sup> Assignment of proton NMR chemical shifts of poly (cyclohexene sulfone) has been made.<sup>51</sup> The absence of appreciable dielectric dispersion of poly (cyclohexene sulfone) solutions indicates that the two sulfone groups attached to the cyclohexane ring are in axial-axial conformation.<sup>61</sup>



The methylene protons beta to the sulfone group have been shown to be non-equivalent by the fine structure in the NMR spectrum of solutions of alpha-deuterated poly (cyclohexene sulfone).<sup>61</sup> Variation in the main chain proton resonances with preparation temperature led to the assumption of tacticity effects in the chain and "isotactic" and "syndiotactic" dyads were postulated. In the isotactic placement, (1-55), the cyclohexane rings were visualized to be placed on the same side of the chain; in syndiotactic placement, (1-56), on opposite sides.<sup>61</sup>



(1-55)



(1-56)

## II. EXPERIMENTAL

### IIa. Chemicals

#### Monomers

Cyclohexene  
Sulfur Dioxide, anhydrous  
grade

#### Source

Eastman Organic Chemicals  
Matheson Company

#### Initiators

t-Butyl Hydroperoxide  
Di-t-Butyl Peroxide  
Cumene Hydroperoxide  
Hydrogen Peroxide  
Silver Nitrate  
Sodium Salt of t-Butyl Hydro-  
peroxide  
Benzoyl Peroxide  
Potassium Persulfate

Matheson, Coleman & Bell  
Wallace and Tiernan  
Matheson, Coleman & Bell  
Mallinckrodt Chemical Works  
Mallinckrodt Chemical Works  
Prepared in this study\*  
Matheson, Coleman & Bell  
Baker Chemical Company

#### Solvents

#### Polymerization and Electronic Spectroscopy

Dichloromethane  
Chloroform  
n-Hexane  
Chlorobenzene  
Acetone  
Toluene  
Cyclohexanone

Reagent Grade from Stock  
Reagent Grade from Stock  
Baker Chemical Company  
Matheson, Coleman & Bell  
Reagent Grade from Stock  
Reagent Grade from Stock  
Eastman Organic Chemicals

#### Polymer Precipitation and Washing

Skellysolv B  
Methanol

Reagent Grade from Stock  
Reagent Grade from Stock

#### Polymer Characterization

Deuteriochloroform  
Tetrahydrofuran

Nuclear Magnetic Resonance  
Specialties  
Fisher Scientific Company

\* Prepared according to directions of Milas and Surgenor<sup>105</sup>



## IIb. Purification of Monomers

Cyclohexene was purified by refluxing over sodium for 24 hours and distillation under nitrogen. The middle 50% of the distillate (boiling point 82.5-83.5°C) was retained and stored over sodium hydroxide. Prior to each polymerization experiment this purified monomer was again refluxed over sodium metal for approximately one hour. The quantity of cyclohexene required for the polymerization was distilled into a receiver and charged to the polymerization vessel by means of a gas tight one ml syringe. This procedure was used to assure the absence of peroxides in the monomer. Sulfur dioxide was obtained by distillation from the cylinder and was used without further purification. Gas chromatographic analysis of the purity of the monomers gave the following results:

### Analysis of Monomers by Gas Chromatography

Monomer	Column Packing	Support	Column Temp., °C	% Purity
Cyclohexene	Apiezon N	Chromosorb P	35	99.5
Sulfur Dioxide	Poropak Q	-	70	99.7

## IIc. Purification of t-Butyl Hydroperoxide

The initiator used in polymerization experiments was purified by preparing the sodium salt of the hydroperoxide

and recovering the purified reagent by acidifying with  $\text{KHSO}_4$  according to the procedure of Milas and Djokis.<sup>106</sup> Analysis of initiator purity was performed by measuring the infrared absorption of a solution of the hydroperoxide in carbon tetrachloride at  $3552\text{ cm}^{-1}$ . Using this procedure, described by Goddu,<sup>107</sup> the purity of the t-butyl hydroperoxide was found to be 90.1%. Chromatographic assay of the hydroperoxide was attempted using an Apiezon N column. Irreproducible results were obtained due to degradation of the hydroperoxide in the column even at ambient injection port and column temperatures.

#### IId. Purification of Dichloromethane

This solvent was shaken with four successive portions of sulfuric acid. The last acid wash was colorless. The dichloromethane was then washed with water, 5% aqueous sodium bicarbonate and water, dried with calcium chloride and distilled from phosphorus pentoxide. The solvent was stored in a brown bottle over Linde 4A molecular sieves. During the experimental determination of reaction kinetics, several experiments were found to be severely inhibited. Since the inhibition was no longer observed when freshly purified dichloromethane was used, the inhibition was attributed to an impurity

accidentally introduced into the solvent. No detailed investigation of the cause of inhibition was undertaken since good replication of kinetic data was found between experiments conducted with the new solvent and the old solvent prior to occurrence of the phenomenon (Runs 51.01 and 56.09). No impurity peaks were detectable in gas chromatographic analysis of the solvent using an Apiezon N column.

### Ile. Equipment

The following instruments were used in the investigation:

Analysis	Instrument
Electronic Energy Absorption of Solutions	Hitachi-Perkin Elmer UV-VIS Spectrophotometer, Model 139
Recording of Photocell Output Current	Bausch & Lomb VOM 7 Laboratory Recorder
Reaction Temperature	Leeds & Northrup Speedomax W with Chromel-Alumel Thermocouple
Chromatographic Analysis	Varian Series 1520 Gas Chromatograph
Infrared Analysis	Perkin-Elmer Model 257 Infrared Spectrophotometer
Molecular Weight and Distribution	Waters Gel Permeation Chromatograph, Model 200
Nuclear Magnetic Resonance	Hitachi-Perkin-Elmer R-24 60 MHz NMR Spectrophotometer



Cuvettes used in the spectrophotometric studies, and in which most of the polymerizations were conducted, were constructed of 10 mm I.D. square Spectrosil fused quartz tubing (Thermal American Fused Quartz Co.). To permit closure of the tops of the cuvettes by a serum cap, a 3 cm long, circular cross section quartz tube was fused onto the 4.5 cm long, square cuvette. The optical path lengths of the two cuvettes used in the study were obtained by calibration with standard  $K_2Cr_2O_7$  solution and were found to be  $9.91 \pm 0.11$  mm. A drawing of the cell holder constructed to maintain the cuvettes at a low temperature in the Hitachi-Perkin-Elmer Spectrophotometer is given in Figure 1 and a schematic sketch of the experimental equipment used to conduct the spectrophotometric kinetic studies is presented in Figure 2.

#### IIIf. Extinction Coefficients of Reagents

Standard photometric technique was used to determine the extinction coefficients of freshly distilled cyclohexene and purified t-butyl hydroperoxide at room temperature. The extinction coefficients of sulfur dioxide solutions were obtained by the following procedure. A serum capped cuvette containing a Teflon covered magnetic bar was evacuated and a weighed amount of solvent was injected from a syringe. The cuvette was placed in the

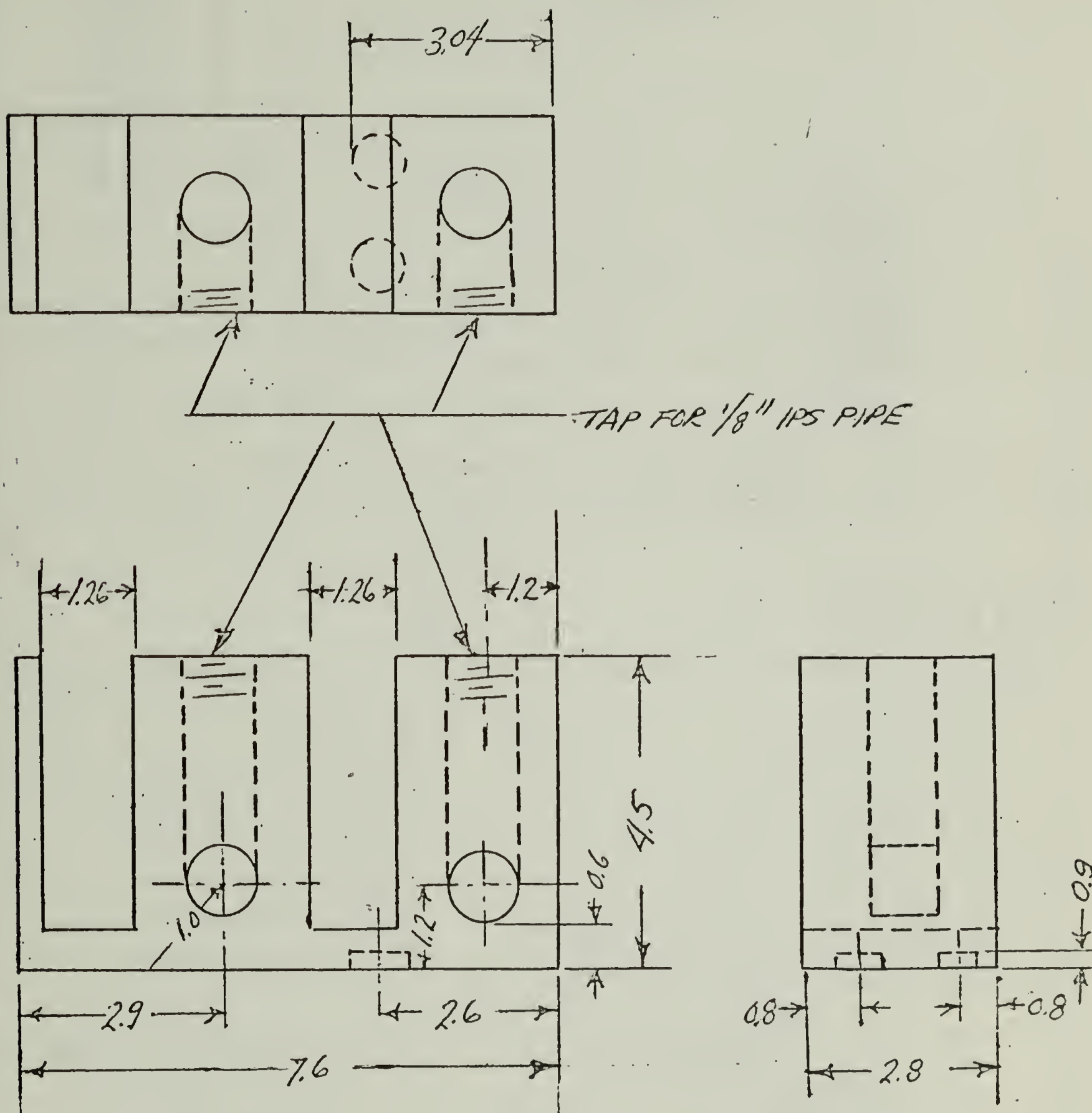


Figure 1. Spectrophotometer cell holder  
 Material of construction: Brass  
 All dimensions in cm

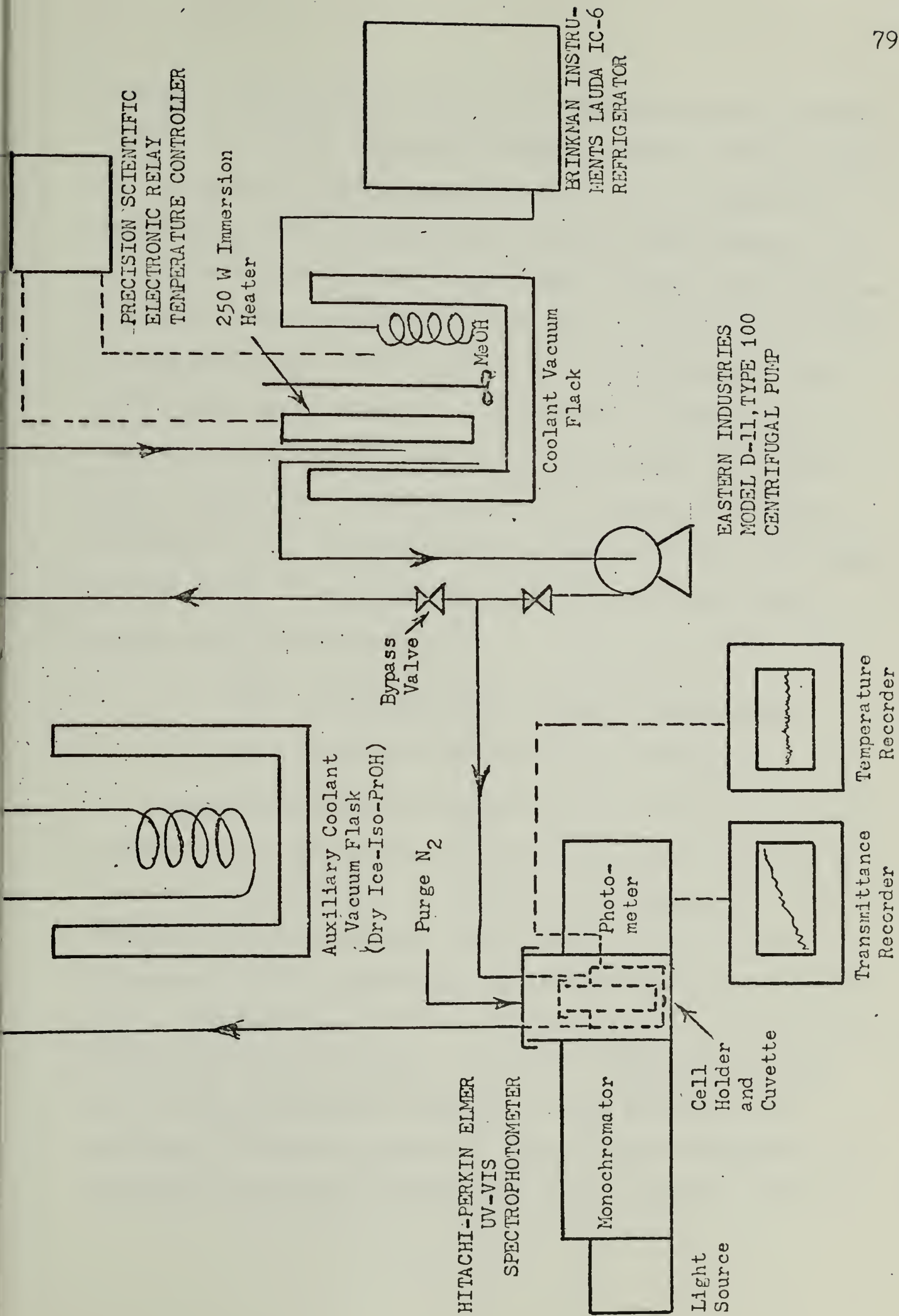


Figure 2. Experimental equipment for spectrophotometric kinetic studies



cooled, thermostated holder, the spectrophotometer sample cavity was purged with dry nitrogen and the transmittance of the solvent determined as a function of wavelength. A known volume of gaseous sulfur dioxide was injected into the cuvette from a one ml gas tight syringe, the solution was mixed and a wavelength scan of the solution was made at the same slit width used in the solvent scan. The extinction coefficient of liquid sulfur dioxide was determined at  $-28^{\circ}\text{C}$  against a dichloromethane reference. Molar extinction coefficients were calculated from the incident, i.e., transmittance through solvent, and transmitted light intensities and the optical path length using the Beer-Lambert law.

### IIg. Charge-Transfer Complex Equilibrium Constant and Extinction Coefficient

Spectrophotometric determination of the equilibrium constants and extinction coefficients were performed in the following manner. A cuvette containing a Teflon covered stirring bar and sealed with a serum cap was evacuated with a hypodermic syringe connected to a vacuum pump. Evacuation of the cuvette was found to be necessary to prevent loss of sulfur dioxide. Approximately three ml of solvent was next charged to the cuvette from a syringe, the exact amount of charge being determined by weighing the syringe before and after charging. The

cuvette was placed in the holder in the spectrophotometer sample cavity, the sample cavity purged with dry nitrogen to prevent condensation and coolant pumped through the sample holder. The spectrophotometer light source was turned on and the system permitted to equilibrate for approximately thirty minutes. The spectrophotometer slit width was kept at a constant setting of 0.9 mm for all transmittance readings. Transmittance readings of the solvent filled cuvette were obtained at 5 nm intervals from 240 to 330 nm. These transmittance values were used as values of the intensity of incident light.

Although the sample cavity was continuously purged with dry nitrogen, it was found desirable to wash off condensation from the face of the cuvette with methanol each time the sample cavity was opened. A gas tight one ml syringe was purged repeatedly with gaseous sulfur dioxide injected into the cuvette. The cuvette contents was agitated by passing a small magnet vertically over the face of the cuvette many times to move the stirring bar inside the cuvette. A scan of the sulfur dioxide solution was made at the same wavelengths and slit settings used in the solvent scan. Approximately 0.3 ml of freshly distilled cyclohexene was injected into the cuvette with a gas tight syringe, the exact weight being determined by weighing the syringe prior to and after

charging. The solution was stirred and the transmittance scanned. Four additional injections of cyclohexene were made and the same mixing and scanning procedure followed after each injection. The coolant temperature was monitored continuously during the experiment and an average temperature inside the cuvette calculated from the average coolant temperature and a calibration of cuvette vs. coolant temperatures. Temperature variation during each experiment was less than  $0.3^{\circ}\text{C}$  at temperatures above  $-40^{\circ}\text{C}$  and less than  $0.9^{\circ}\text{C}$  between  $-55$  and  $-40^{\circ}\text{C}$ .

#### IIh. Densities

Values of densities of the liquid reagents were obtained from the literature. These values were corrected to the temperature of measurement using the generalized expansion factor relationship: 108

$$\rho = \rho_r \left( \frac{0.1745 - 0.0838(T/T_c)}{0.1745 - 0.0838(T_r/T_c)} \right) \quad (2-1)$$

where  $\rho_r$  is the density at  $T_r$ ,  $^{\circ}\text{K}$ ,  $\rho$  is the density at  $T$ ,  $^{\circ}\text{K}$  and  $T_c$  is the critical temperature of the compound. The molar volume of gaseous sulfur dioxide was estimated from the ideal gas law.



### IIIi. Copolymer Composition

Elemental microanalyses were performed by the University of Massachusetts Microanalysis Laboratory using appropriate techniques. Infrared spectra of the copolymers were obtained by casting dichloromethane solutions of the copolymers on NaCl plates, evaporating the solutions in vacuo at room temperature for approximately two hours and scanning the film vs. air on a Perkin-Elmer Model 257 Infrared Spectrophotometer. Nuclear magnetic resonance spectra of approximately 10% solutions of the copolymers in  $\text{CDCl}_3$  were obtained at room temperature on a Hitachi-Perkin-Elmer 60 MHz R-24 NMR Spectrometer. Tetramethylsilane was used as an internal reference.

### IIIj. Molecular Weights

Molecular chain lengths and chain length distributions were determined using Waters Model 200 Gel Permeation Chromatographs at the University of Massachusetts and at DeBell and Richardson, Inc. The following conditions were used in the determinations:

<u>Instrument</u>	<u>Univ. of Mass.</u>	<u>de Bell and Richardson</u>
Solvent	Tetrahydrofuran	Dimethylformamide- 0.1M LiBr
Concentration, %	0.8	0.5
Flow rate, ml/min	1	1
Column type	Polystyrene Gel	Polystyrene Gel
Column pore sizes	$10^6, 10^5, 8.5 \times 10^3, 10^3$	$10^7, 3 \times 10^6, 10^5, 10^3$
Temperature, °C	25	72
Column calibration	Narrow distribution polystyrene	

The molecular chain length calculations were based on calibrations made with essentially monodisperse polystyrene fractions. This assumes similarity of the hydrodynamic diameters of polystyrene and poly (cyclohexene sulfone). Molecular size was reported as chain length rather than molecular weight since the hydrodynamic length of a cyclohexene-sulfone residue, i.e., the Q value, was determined only to very limited precision. Calculation of the number and weight average chain lengths; the first, second and third moments of the distribution; and the cumulative and differential weight distributions vs. chain lengths was performed with the computer program MOLWT. No correction for peak broadening was used in the calculation.

The number average molecular weight of one of the copolymer samples was determined by the University of Massachusetts Microanalysis Laboratory. A Mechrolab Model 302 Vapor Pressure Osmometer was used to obtain the molecular weight of the sample dissolved in chloroform at 37° C.

### IIk. Reaction Kinetic Studies

The course of the polymerization reaction as well as that of the reaction between sulfur dioxide and t-butyl hydroperoxide was followed by measuring solution optical density by visible spectrophotometry and concentrations by gas chromatography.

A Teflon-covered stirring bar was placed in a square quartz cuvette of known optical path length which had previously been cleaned in boiling nitric acid, washed with distilled water and dried in a 150°C oven overnight. The cylindrical top of the cuvette was sealed with a rubber serum cap tightened to the cuvette by wire. Solvent extractable substances had previously been removed from the serum caps by extracting them with dichloromethane for 24 hours in a Soxhlet extractor. The capped cuvette was weighed, placed in a dry ice-isopropanol bath and approximately twice the desired amount of sulfur dioxide was charged from the gas cylinder by allowing the gas to pass through a needle passing through the serum



cap and condense in the cuvette. The excess sulfur dioxide was permitted to evaporate by allowing the needle vented cuvette to warm on the pan of an analytical balance and quickly removing the needle and cooling the cuvette when the desired weight was reached. It was found necessary to wipe the outside of the cuvette periodically during the weighing to remove condensation. Dichloromethane was injected into the cuvette from a syringe, the exact weight charged being determined by weighing the syringe before and after charging.

The cuvette was placed in the nitrogen purged sample holder of the spectrophotometer, the contents mixed by moving the stirring bar in the cuvette with an external magnet, and the light source and sample temperature allowed to equilibrate for 30 minutes. During this period a two to five microliter sample was removed from the cuvette and injected into the gas chromatograph to obtain calibrations of the elution area ratios of the comonomers to the solvent vs. the weight ratios of monomers to solvent. Three duplicate determinations were conducted. The following conditions were used in the chromatographic analysis:

Column: 20% Apiezon N on 80/100 Chromosorb P, 1/8" x 6'

Sample size: 2 microliters

Detector: Thermal Conductivity

Detector Current: 150 ma.

Carrier gas: Helium, 30 ml/min.

Temperatures:

Column: 35°C

Injection port: ambient

Detector: 220°C

Elution times after injection:

Sulfur Dioxide	0.4 min.
Dichloromethane	1.4 min.
Cyclohexene	7.1 min.
Reaction Product from SO <sub>2</sub> and t-Butyl Hydroperoxide	7.2 min.

Polymer did not appear to be eluted during a series of determinations. Polymer remaining on the column was removed by heating the column to 200°C after conclusion of each run.

After washing the cuvette face with methanol to remove any possible condensation, the transmittance of the solution prior to the addition of cyclohexene or t-butyl hydroperoxide was determined. This reading served as the incident light transmittance value for each run. Variation in optical density due to variation in light source output or photocell response did not exceed 0.03 over a 90 minute period.

The polymerization reactions were normally followed spectrophotometrically at a wavelength of 375 nm, although subsidiary readings at 360, 380 and 385 nm were also obtained in some runs. Slit width was maintained at 0.5 mm for these experiments. The reactions between sulfur

dioxide and t-butyl hydroperoxide were followed at 360 nm and a slit width of 0.45 mm. It was not possible to observe the polymerization reaction near the absorption maximum attributable to the charge-transfer complex, 310 nm, due to the high extinction coefficient at the maximum. Decreasing the optical path length, either by insertion of a quartz spacer or by the use of a thinner cuvette, was found to be impractical. It was not possible to agitate the solutions, addition of initiator and sampling of the contents led to unacceptably large changes in the total solution volume and insufficient polymer was prepared to permit characterization. Decreasing the monomer concentration would lead to larger charging errors, increased depolymerization tendency as well as decreasing the amount of polymer produced. Optical density determinations were therefore made on the slope of the charge-transfer complex absorption band where the extinction coefficient is sufficiently low to permit determinations in the range of less than 2% relative error, i.e., optical densities between 0.1 and 1.0, to be carried out at the concentrations used. The equivalence of the enthalpy of complex formation determined from observations at the absorption maximum and at 375 nm demonstrates that no appreciable error is introduced by not conducting the measurements at the absorption maximum.



In polymerization experiments, the desired quantity of freshly distilled cyclohexene was injected into the cuvette, the exact amount being determined from the differential weight of the charging syringe. The transmittance of this solution was measured. This value is related to the concentration of the charge-transfer complex prior to the start of the polymerization. The desired charge of t-butyl hydroperoxide was then made by injecting into the serum capped cuvette. The weight of initiator charged was determined from the differential weight of the full and empty syringe. The time of initiator charge was defined as the initial time of the reaction.

Immediately after charging the initiator, the solution was stirred manually for approximately 30 sec. with the external magnet, the cuvette face washed with methanol, the sample holder cover replaced, the photocell shutter opened and the transmittance of the solution recorded instrumentally vs. time. Frequent checks of the photocell dark current were made throughout the run by closing the shutter. At approximately ten minute intervals a sample of the cuvette contents was removed with a microliter syringe and injected into the gas chromatograph for analysis of the components. It should be pointed out that sampling of the reaction mixture became more difficult with increasing sulfur dioxide concentration since pressure

exerted by the dissolved sulfur dioxide in the warm syringe tended to force liquid out of it. This placed a practical upper limit of approximately one on the molar ratio of sulfur dioxide to cyclohexene in the experimentally attainable monomer charges. The contents of the cuvette was stirred and the cuvette face was washed with methanol each time a sample was removed for chromatographic analysis. The runs were continued until no change in transmittance of the solution with time was evident, normally 60-70 minutes.

Temperature of the reaction was controlled with on-off control of electrical power to an immersion heater located in the methanol coolant reservoir. The addition of dry ice to an auxiliary cooling reservoir containing a cooling coil was required to achieve temperatures below approximately  $-15^{\circ}\text{C}$ . The temperature of the coolant at the sample holder was recorded continuously during each experiment and the internal temperature of the cuvette was calculated from the coolant temperature using a previously determined calibration between temperatures at the two points. The standard deviation of the time variation of temperature from the average temperature reported for each run averaged  $0.4^{\circ}\text{C}$ , ranging from  $0.1$  to  $0.9^{\circ}\text{C}$  for the individual runs.

After the completion of each polymerization run, the

solution contained in the reaction cuvette was diluted approximately threefold with dichloromethane, the polymer precipitated in Skellysolv B, (a mixture of hexanes, heptanes, octanes and solvent naphtha), filtered on a sintered glass filter, washed with methanol and dried in vacuo at room temperature for 24 hours. Polymer yield was obtained by weighing this dried sample. Further purification of each sample was performed by redissolving, reprecipitating, rewashing and redrying the polymer. The surface of the polymer was colored prior to washing with methanol; the color ranging from light yellow to brown. Repeated methanol washing removed this color completely. The final dried sample was an amorphous white powder. Precipitation in methanol was found to be impractical since a very fine precipitate was formed which passed through the filter.

The molar concentrations of the comonomers and initiator, the ratio of these concentrations to that of the solvent, the polymer yield and average temperature and time average standard deviation were calculated using the computer program INCIN. Inputs to the program were weights of reagents and product, thermocouple voltage readings and zero setting and span of the temperature recorder. Volume at the temperature of measurement was



calculated assuming additive volumes of reagents and reagent densities corrected for temperature.

The contribution to the optical density due to the charge-transfer complex was calculated from the differences between the photometer light and dark current readings which are proportional to the solution transmittances. The computer program RAWDAT was used to calculate the optical density, corrected for absorption by the reagents and dilution of the sulfur dioxide after the cyclohexene charge, referred to the solution of sulfur dioxide in dichloromethane. Data required for the calculation are the extinction coefficients of sulfur dioxide and t-butyl hydroperoxide at the wavelength of measurement, the sulfur dioxide concentration prior to the cyclohexene charge and after the initiator charge, the initiator concentration, the spectrophotometer attenuation factor and light and dark current readings for each of the measurements made during the run and prior to the start of the reaction. No correction for the optical absorption of cyclohexene was made since its extinction coefficient at the wavelengths of measurement was determined to be negligible. Similarly, no correction for the absorption of the polymer was made, since aliphatic sulfones have been found to be transparent at wavelengths greater than 200 nm. 109

### III. RESULTS AND DISCUSSION

#### IIIa. Extinction Coefficients of Reagents

The extinction coefficients of the reagents used in the investigation are presented in Figure 3. The coefficient of cyclohexene was not measurably affected by a variation in concentration from three to ten molar nor by temperature variation from -60 to 25°C. No temperature effect on the sulfur dioxide extinction coefficient was observed between -2 and -34°C.

The electronic absorption spectrum of sulfur dioxide shows two absorption regions with maxima at 362 and 290 nm. The start of a third, higher energy absorption band whose maximum occurs at less than 200 nm is evident.<sup>34</sup> The extinction coefficient in the non-polar solvent, n-hexane, is slightly less than that found in the more highly polar solvent, dichloromethane. The extinction coefficient at the absorption maximum, 290 nm was found to equal  $318 \text{ l mol}^{-1} \text{ cm}^{-1}$  in n-hexane and 446 in dichloromethane. Standard deviations of these values were found to be  $10 \text{ l mol}^{-1} \text{ cm}^{-1}$ . These determinations compare with extinction coefficients of 342 in n-hexane,<sup>34</sup> 317 in n-heptane,<sup>33</sup> 328 in cyclohexane (at 292 nm) and 350 in chloroform (at 289 nm)<sup>30</sup> found by other investigators.

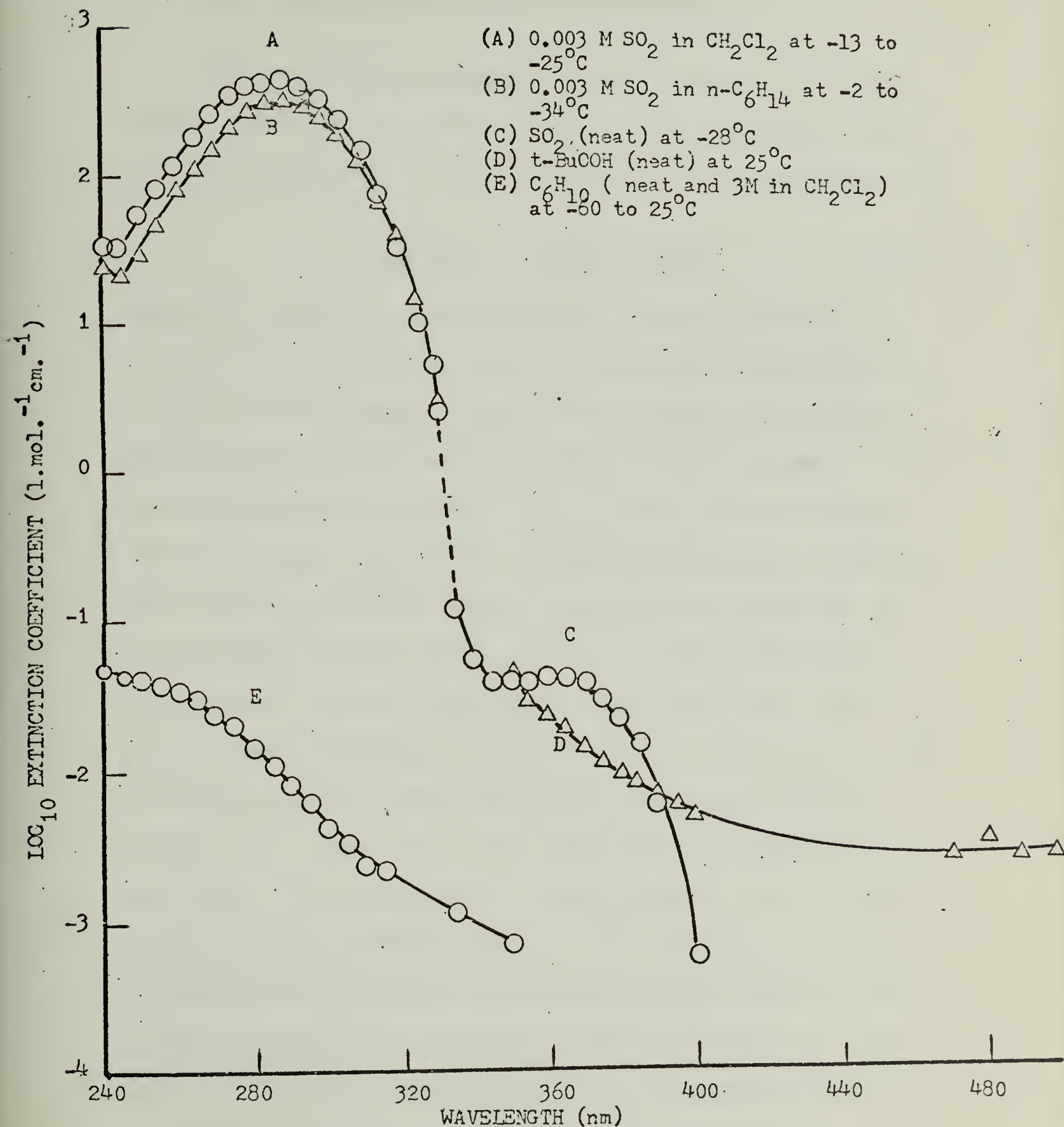


Figure 3. Extinction coefficients of reagents



### IIIb. Equilibrium Constant Determination

The relationship between optical density of a solution containing an electron donor and an acceptor and the concentrations of the components may be expressed as:

$$\frac{\Delta OD}{[D]_0 [A]_0} = -K_c \frac{\Delta OD}{[A]_0} + K_c \Delta \epsilon \quad (3-1)$$

where  $[A]_0$  and  $[D]_0$  are the molar concentrations of acceptor and donor respectively, neglecting dissociation,  $\Delta \epsilon$  is the difference in extinction coefficient between the complex and the acceptor (which absorbs light at the wavelength of measurement),  $\epsilon_c - \epsilon_A$ ,  $\Delta OD$  is the measured optical density corrected for absorption of the acceptor for unit optical path length, equal to the measured optical density minus  $\epsilon_A [A]_0$ , and  $K_c$  is the equilibrium constant of complex formation. Equation (3-1), the Foster-Hammick-Wardley equation,<sup>110</sup> is equivalent to the Ketelaar equation and applies under the same restrictions, i.e.,  $[D]_0 \gg [A]_0$  and negligible absorption by the donor. This equation is preferable to the Ketelaar equation since determination of the constants involves extrapolation to dilute concentration and, since the acceptor concentration appears in both dependent and independent variables, data points from determinations made at different acceptor concentrations can be used.

The molar concentration of the donor, cyclohexene, was calculated from the weights of solvent and cyclohexene charged and the extrapolated densities at the temperature of measurement assuming additive volumes. Since the concentration of sulfur dioxide was determined from the optical density of the solution at 290 nm prior to the addition of cyclohexene, the Foster-Hammick-Wardley equation was modified to substitute the optical density of the sulfur dioxide solution at 290 nm, the absorption maximum, as a variable instead of the sulfur dioxide concentration,  $[A]_0$ :

$$\frac{\Delta OD}{[D]_0 (OD'_a)} = -K_c \frac{\Delta OD}{(OD'_a)} + K_c \frac{\Delta \epsilon}{\epsilon'_a} \quad (3-2)$$

$OD'_a$  is the measured optical density of the initial sulfur dioxide solution at 290 nm extrapolated to account for dilution by the cyclohexene (by multiplying the ratio of solvent volume to volume under the conditions of the equilibrium constant determination). The extinction coefficient of sulfur dioxide at 290 nm is given by the term  $\epsilon'_a$ . In this procedure it is assumed that the extinction coefficient of sulfur dioxide in the solvent would remain essentially unchanged if no complex formation were to take place upon the addition of donor. The assumption is reasonable since the experimental solvent concentrations greatly exceeded the donor concentrations. If  $\frac{\Delta OD}{[D]_0 (OD'_a)}$

is plotted against  $\frac{\Delta OD}{(OD)_a}$  a straight line should be obtained. The equilibrium constant is equal to the negative slope of the line and the extinction coefficient of the complex is given by the expression:

$$\epsilon_c = \frac{I}{s} \epsilon_a' + \epsilon_A \quad (3-3)$$

where  $I$  and  $s$  are the intercept and slope of this line respectively.

Experimental data are plotted in Figure 4 according to equation (3-2) for solutions in n-hexane at 300 nm. The assumption of equimolar complex formation is confirmed by the linearity of these plots. Numerical values of the intercepts,  $K_c \Delta \epsilon / \epsilon_a'$  and the slopes,  $-K_c$ , of determinations made at constant temperature were evaluated by least squares bivariate regression analysis. These values for wavelengths near the absorption maxima, 290, 295, 300, 305 and 310 nm, and the standard deviations of the values, are presented in Table II for n-hexane solutions and Table III for dichloromethane solutions. Inspection of these values shows that the intercept is evaluated more precisely than the slope. This lack of precision in the mathematical separation of  $K_c$  from the more precise  $K_c \epsilon_c$  product was pointed out by Foster.<sup>111</sup> Since the measured optical density (when  $[D]_0 \gg [A]_0$  and the components do not absorb) may be expressed as:



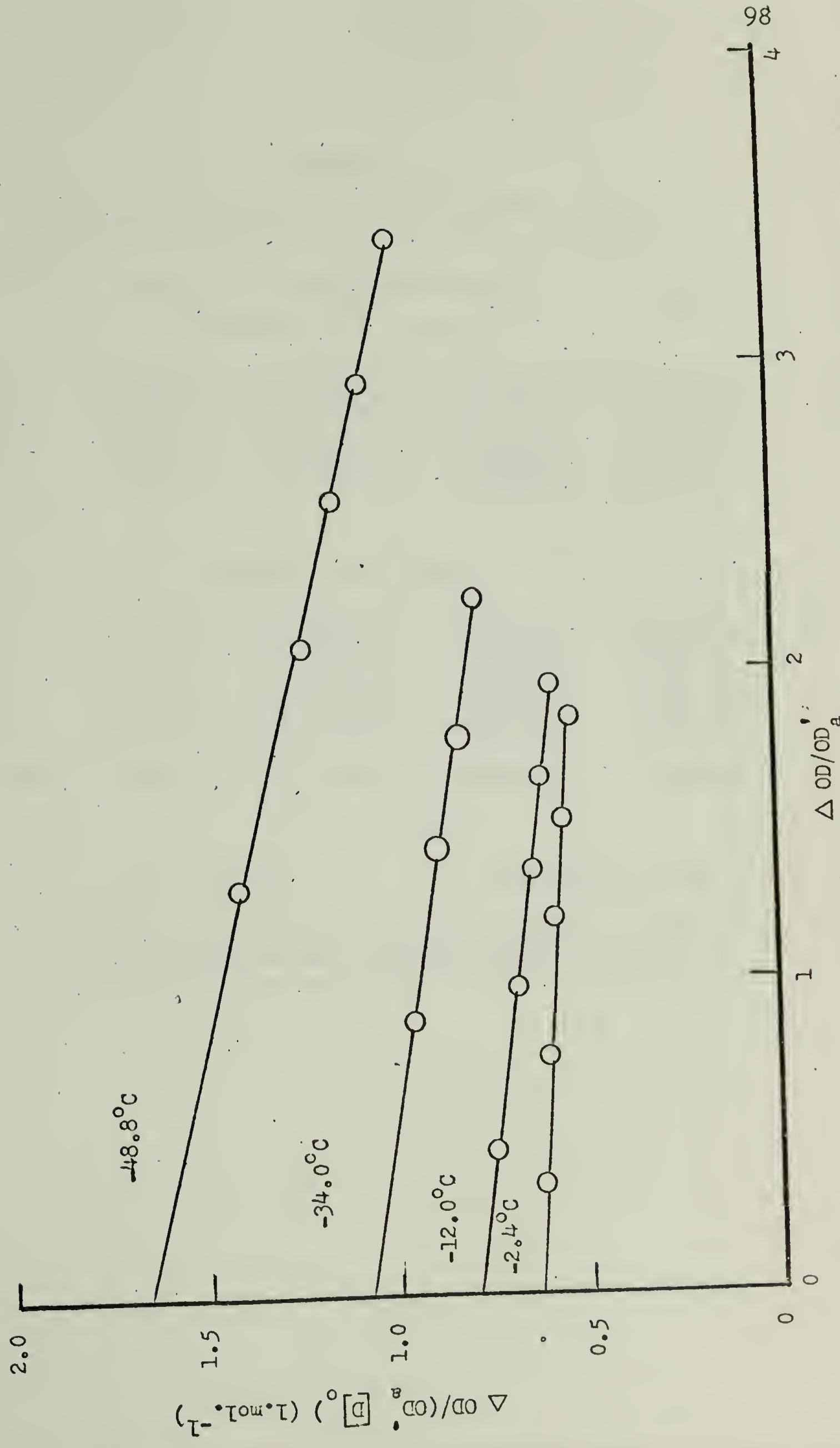


Figure 4. Evaluation of equilibrium constant and extinction coefficient of cyclohexene-sulfur at 300 nm

TABLE II  
Slopes, Intercepts and Standard Deviations of Modified  
Foster-Hammick-Wardley Plots for n-Hexane Solutions

Wavelength, nm	Temperature, °C			
	-48.8	-34.0	-12.0	-2.4
	Intercept x 10 = $10K_c \Delta\epsilon/\epsilon'_a$			
290	13.61 $\pm$ 0.19	8.90 $\pm$ 0.17	7.16 $\pm$ 0.17	5.06 $\pm$ 0.08
295	15.00 $\pm$ 0.17	10.05 $\pm$ 0.05	7.64 $\pm$ 0.13	5.78 $\pm$ 0.08
300	16.49 $\pm$ 0.27	10.09 $\pm$ 0.12	8.01 $\pm$ 0.10	6.25 $\pm$ 0.13
305	17.10 $\pm$ 0.23	10.91 $\pm$ 0.22	7.84 $\pm$ 0.13	6.48 $\pm$ 0.17
310	15.37 $\pm$ 0.16	9.89 $\pm$ 0.15	6.49 $\pm$ 0.18	6.17 $\pm$ 0.15
	Slope x -100 = $100K_c$			
290	18.12 $\pm$ 0.74	11.81 $\pm$ 1.04	11.89 $\pm$ 1.04	5.74 $\pm$ 0.51
295	18.55 $\pm$ 0.62	13.79 $\pm$ 0.29	12.05 $\pm$ 0.76	6.61 $\pm$ 0.48
300	19.39 $\pm$ 0.89	13.86 $\pm$ 0.63	11.22 $\pm$ 0.53	5.83 $\pm$ 0.74
305	19.22 $\pm$ 0.73	12.76 $\pm$ 1.10	9.44 $\pm$ 0.67	3.83 $\pm$ 1.01
310	16.11 $\pm$ 0.53	10.39 $\pm$ 0.81	4.07 $\pm$ 0.99	3.10 $\pm$ 0.96
Average Slopes	18.28 $\pm$ 1.31	12.52 $\pm$ 1.46	11.47 $\pm$ 1.19	6.00 $\pm$ 0.48

0.6-3.4 M C<sub>6</sub>H<sub>10</sub>

0.0014-0.0028 M SO<sub>2</sub>

Values greater than 3 standard deviations removed from average values of slopes were not used in calculating the averages.

TABLE III

Slopes, Intercepts and Standard Deviations of Modified  
Foster-Hammick-Wardley Plots for Dichloromethane Solutions

Wave length nm	Temperature, °C					
	-56.3	-50.7	-46.6	-33.2	-28.5	-13.0
Intercept x 10 = $10K_c \Delta\epsilon/\epsilon'_a$						
290	4.43±0.04	4.05±0.13	4.08±0.05	3.38±0.01	3.30±0.03	2.63±0.02
295	5.29±0.03	4.97±0.15	4.98±0.03	4.04±0.04	4.11±0.03	3.26±0.02
300	6.29±0.07	6.33±0.24	5.90±0.05	4.70±0.06	4.67±0.06	3.71±0.04
305	7.29±0.06	6.76±0.23	6.88±0.09	5.21±0.07	4.61±0.21	3.95±0.14
310	8.11±0.07	7.20±0.23	7.15±0.08	5.37±0.07	5.27±0.26	4.08±0.06
Slope x -100 = $100K_c$						
290	2.77±0.33	1.45±1.16	2.63±0.40	2.66±0.10	1.88±0.37	2.91±0.27
295	2.92±0.21	2.93±1.13	4.14±0.19	3.41±0.31	3.71±0.34	4.27±0.58
300	2.70±0.41	5.14±1.49	4.54±0.29	3.03±0.42	2.76±0.48	3.07±0.38
305	3.15±0.31	3.28±1.24	5.87±0.51	3.21±0.40	-1.50±1.52	1.70±1.22
310	4.08±0.32	3.84±1.21	5.04±0.39	2.86±0.38	4.83±1.84	1.85±0.50
Avg. Slopes	3.12±0.56	3.32±1.23	4.45±1.20	3.08±0.32	3.24±0.68	3.40±0.61

0.8-3.8 M  $C_6H_{10}$ 0.0011-0.025 M  $SO_2$ 

Values further than 3 standard deviations removed from average  
values of slopes were not used in calculating the averages.



$$OD = K_c \epsilon_c [A]_0 [D]_0 - K_c (OD) [D]_0, \quad (3-4)$$

the effect of the normally high complex extinction coefficient is to increase the importance of the first term in the control of the optical density. To arrive at the best estimate of the equilibrium constant, the average value of this constant was obtained from the experimentally determined constants at the five wavelengths from 290 to 310 nm. From these wavelength averaged values, a mean value of the equilibrium constant corrected for temperature was found by least squares analysis of the variation of the average equilibrium constant with temperature, i.e., determining the average values of the constant and the experimental temperature from a van't Hoff plot of the data.

The best estimate of the equilibrium constant in n-hexane solutions was found to be  $0.112 \text{ l mol}^{-1}$  at  $-25.6^\circ\text{C}$ . For dichloromethane solutions the best estimate of the equilibrium constant was  $0.034$  at  $-34.4^\circ\text{C}$ . The wavelength averaging of the equilibrium constant assumes that the constant does not vary with wavelength. Equilibrium constant variation with wavelength would occur if more than one complex species (e.g., AD and  $AD_2$ ) were present in the solution or if appreciable contact charge-transfer absorption existed.<sup>112</sup> The rather large

deviation of the experimentally determined values of  $K_c$  precluded evaluation of these possibilities.

### IIIc. Thermodynamic Constants of Complex Formation

The van't Hoff equation:

$$d \ln K_c / d(1/T) = -\Delta H^\circ / R \quad (3-5)$$

was used to find the enthalpy of formation of the complex by determining the slopes from the least squares linear regression of  $\ln (K_c \Delta \epsilon / \epsilon_a')$  vs.  $1/T$ . The best estimate of the enthalpies of formation was obtained by averaging the slopes of the five determinations at wavelengths from 290 to 310 nm. The relation between the modified Foster-Hammick-Wardley intercepts and temperature is exemplified by the curves of Figure 5. The enthalpy of formation determined in this manner is independent of the absolute value of the equilibrium constant, but does depend on the assumption of temperature independence of the extinction coefficient term,  $\Delta \epsilon / \epsilon_a'$ , which is usually true within the precision of the data.<sup>111</sup> The free energy of complex formation was obtained from the best estimate of the equilibrium constant at the average of the experimental temperatures found from the slopes of the modified Foster-Hammick-Wardley plots. Entropies of formation were determined from the free energies and enthalpies of formation.

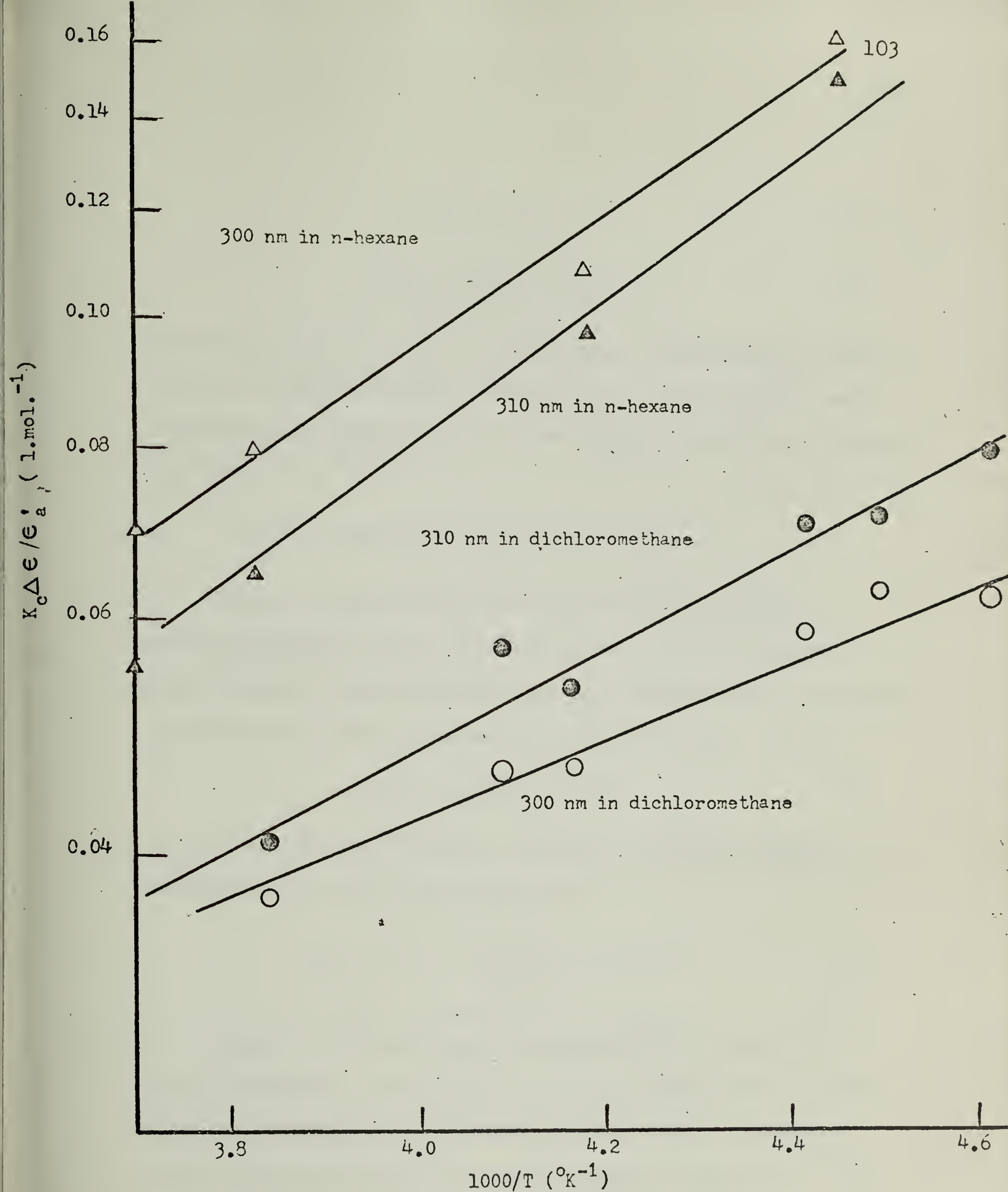


Figure 5. Effect of temperature on  $K_c \Delta \epsilon / \epsilon'_a$



$$\Delta F^{\circ} = -RT \ln K_c \quad (3-6)$$

$$\Delta S^{\circ} = (\Delta H^{\circ} - \Delta F^{\circ})/T \quad (3-7)$$

Numerical values of the thermodynamic constants in n-hexane and dichloromethane obtained from this analysis are presented and compared to those obtained by Booth, Dainton and Ivin<sup>34</sup> in Table IV.

#### IIIId. Absorption Spectrum of Complex

Plots of the intercepts of the modified Foster-Hammick-Wardley plots vs. reciprocal absolute temperature provided the data required to evaluate the extinction coefficient of the complex from 240 to 330 nm. Since:

$$\ln K_c = \Delta S^{\circ}/R - \Delta H^{\circ}/RT \quad (3-8)$$

and, from the relationship between the Foster-Hammick-Wardley intercepts and temperature:

$$\ln K_c = \left( I - \ln \frac{\epsilon_c - \epsilon_A}{\epsilon'_a} \right) - \Delta H^{\circ}/RT, \quad (3-9)$$

$$\epsilon_c = \epsilon'_a \exp(I - \Delta S^{\circ}/R) + \epsilon_A \quad (3-10)$$

where I is the Foster-Hammick-Wardley intercept.

The wavelength variation of the complex extinction coefficient in n-hexane and dichloromethane and a comparison with values determined by Booth, Dainton and Ivin<sup>34</sup> are presented in Figure 6.

TABLE IV

Thermodynamic Constants of Complex  
Formation and their Standard Deviations

Solvent	Experimental Values		Literature Value <sup>34</sup>
	CH <sub>2</sub> Cl <sub>2</sub>	n-Hexane	n-Hexane
Temp. Range, °C	-13 to -56	-2 to -49	+15 to +40
Wavelength, nm	290 to 310	290 to 310	250
$\Delta F^\circ$ , kcal mol <sup>-1</sup>	$1.60 \pm 0.09$	$1.08 \pm 0.05$	$1.74 \pm 0.01$
Temp. of $\Delta F^\circ$ evaluation	-34.4°C	-25.7°C	+25°C
$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$-1.46 \pm 0.22$	$-2.34 \pm 0.23$	$-0.80 \pm 0.05$
$\Delta S^\circ$ , cal mol <sup>-1</sup> deg <sup>-1</sup>	$-12.9 \pm 1.3$	$-13.8 \pm 1.1$	$-8.5 \pm 0.2$

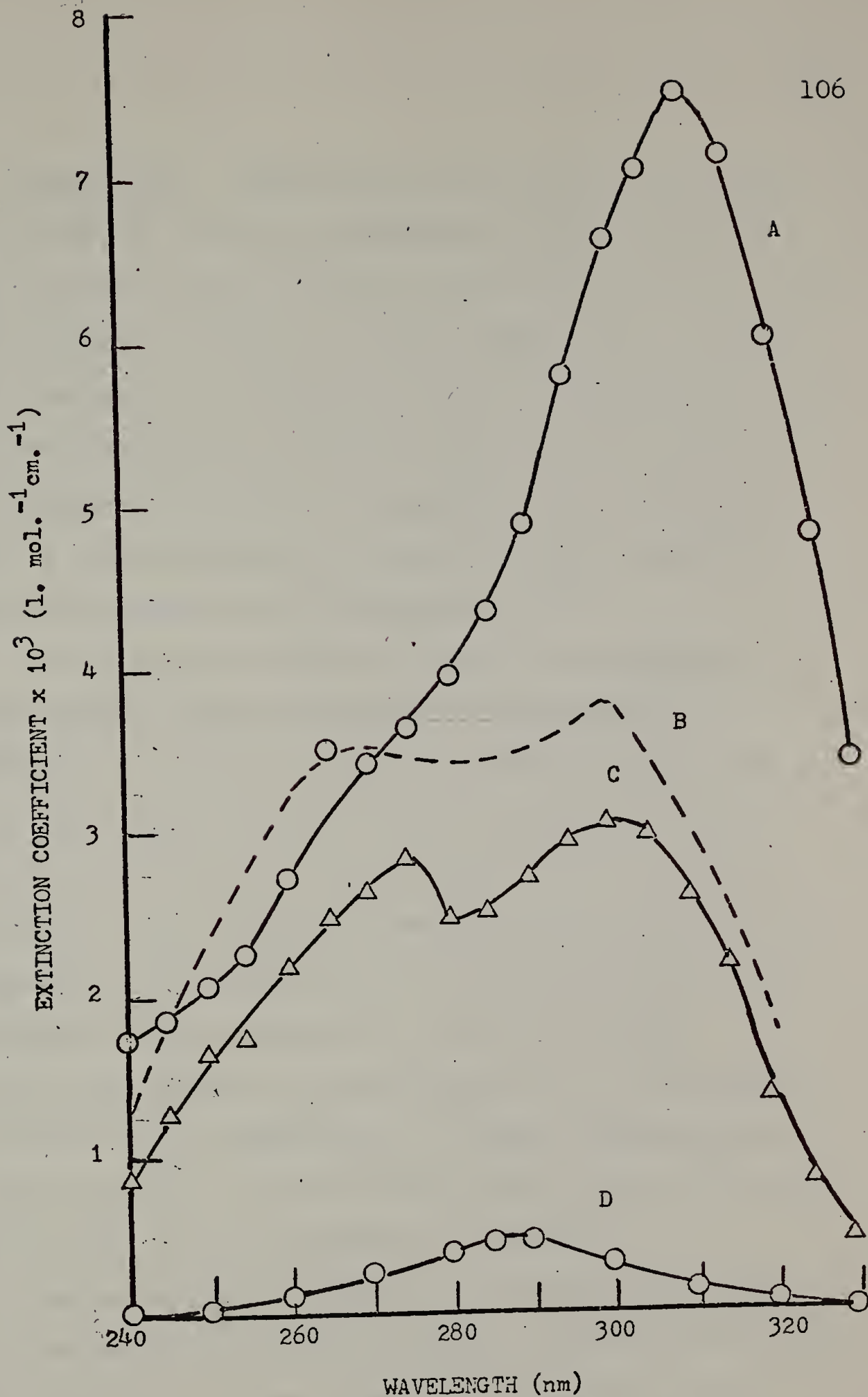


Figure 6. Extinction coefficient of cyclohexene-sulfur dioxide charge-transfer complex  
 (A) Complex in dichloromethane  
 (B) Complex in n-hexane, literature results  
 (C) Complex in n-hexane, this work  
 (D) Sulfur dioxide in dichloromethane



Discussion. Comparison of the values of enthalpy and entropy of formation determined in this work with those found by Booth, Dainton and Ivin<sup>34</sup> shows that both thermodynamic constants are higher than those reported in the literature. Although this may be attributable to the different temperature ranges used in the investigations, differences of the order of magnitude shown are not unusual in determinations of charge-transfer properties made by two groups of investigators.<sup>113</sup>

The enthalpy of complex formation in n-hexane is significantly higher than that in dichloromethane (evaluated by Student's t test at 99% confidence level). Decreasing complex stability with increasing solvent polarity has frequently been observed and has been attributed to competition in complex formation between one component of the complex and the solvent and/or to stabilization of the complex in a non-polar medium.<sup>7</sup> In light of the observed slight interaction of chlorinated solvents and the components,<sup>33</sup> complex stabilization in n-hexane appears to be the most probable cause of the observed difference in enthalpy of formation.

The absorption spectrum of the complex in n-hexane shows maxima at both 275 and 300 nm. Booth, Dainton and Ivin ascribed the lower wavelength transition to the charge-transfer complex since their study showed a

correlation of the energy of this transition with the electron donating capability, i.e., ionization potential, of a series of electron donors. The second absorption band was attributed by these investigators to a transition of uncomplexed sulfur dioxide, decreased in energy due to the proximity of donor or complex molecules. In dichloromethane, the lower wavelength band, although still present, is not as distinct due to increased overlap from the more intense high wavelength band. The decreased energy of the high wavelength transition in dichloromethane compared to that in n-hexane may be attributable to stabilization of the ground state of this transition in the solvent of higher polarity. The enhanced extinction coefficient observed in dichloromethane appears to be a reflection of the approximate constancy of the measured values of the product  $K_c \epsilon_c$  in the two solvents.

#### IIIe. Enthalpy of Complex Formation from High Concentration Data

The corrected optical densities of solutions of sulfur dioxide and cyclohexene in dichloromethane were determined at 375 nm prior to the addition of t-butyl hydroperoxide during the exploration of the polymerization reaction at  $-19^\circ\text{C}$ . The temperature variation of the complex

optical density in these concentrated solutions serves as an additional determination of the enthalpy of formation of the charge-transfer complex. Data are plotted against the reciprocal of absolute temperature in Figure 7. The enthalpy of formation of the complex estimated from the slope of the least squares line through the points was found to equal  $-1.48 \pm 0.17$  kcal/mole, well within the limits of error of the value determined in the low concentration runs. The good agreement in values of the enthalpy of formation in experiments conducted near the absorption maximum and on the slope of the absorption band, and with a 300 fold variation in sulfur dioxide concentration, demonstrates that the same phenomenon is observed in both measurements.

### IIIIf. Copolymer Composition

IIIIf1. Elemental analysis. Elemental analysis of copolymer samples are presented in Table V together with a summary of the polymerization conditions. The copolymer composition appears to be independent of the starting comonomer composition, total comonomer concentration, initiator concentration, purity of cyclohexene and polymerization temperature within the range of experimentation. Comparison of the averages of the individual elemental analyses with the theoretical values for alternating 1:1



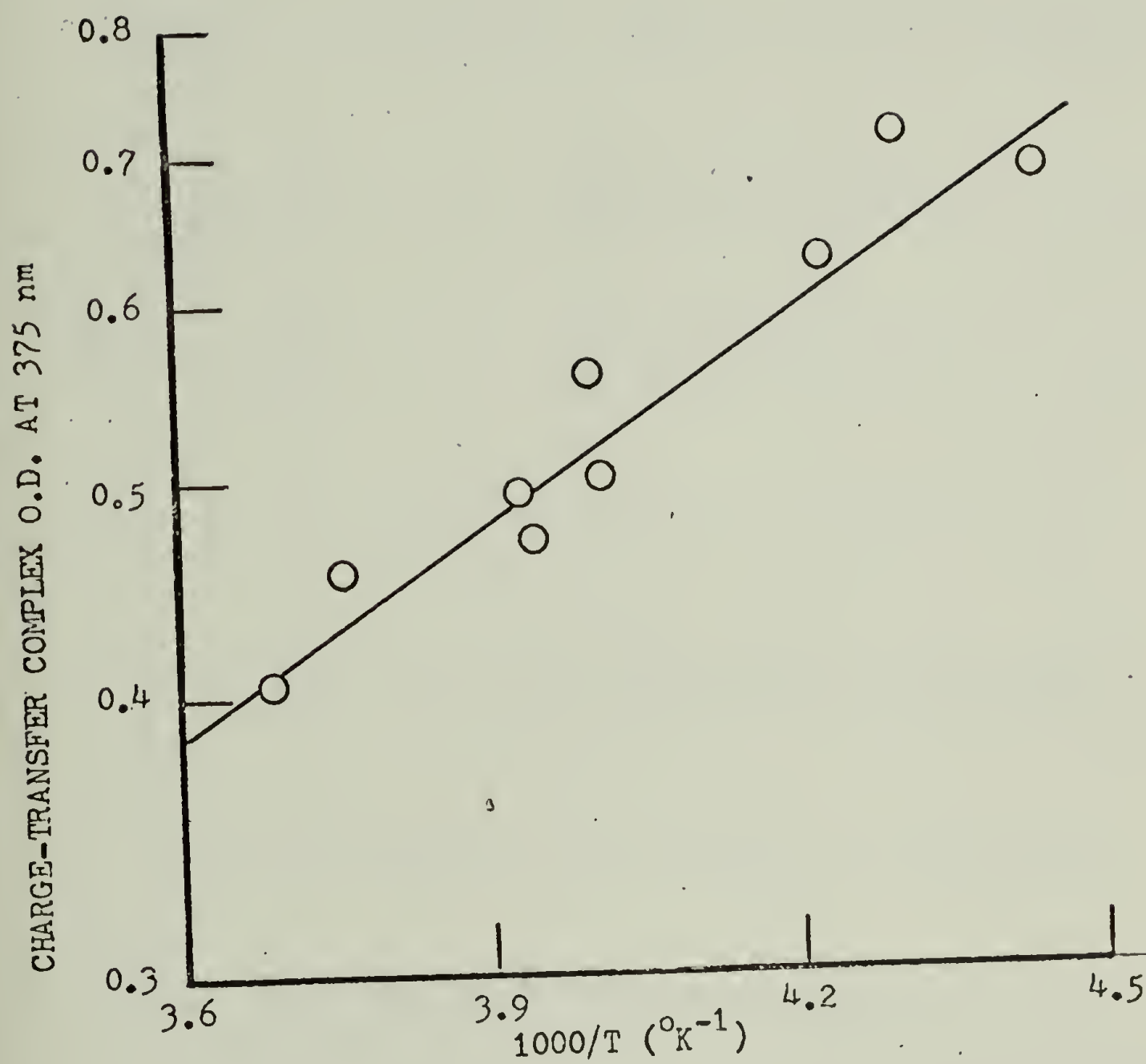


Figure 7. Evaluation of enthalpy of charge-transfer complex formation at high sulfur dioxide concentration  
 Sulfur dioxide concentration =  $0.65 \text{ mol.l.}^{-1}$   
 Cyclohexene concentration =  $3.3 \text{ mol.l.}^{-1}$

TABLE V

Copolymer Composition of Poly(Cyclohexene Sulfone) Prepared in Dichloromethane

Run Ident.	$x_D^1$	$[S]_0$	$[I]_0$	Temp., °C	Elemental Analysis			$d[D]/d[S]_{\text{calc.}}$ from	
					%C	%H	%S	%Cl	%S    %C
10.2 <sup>2</sup>	0.841	1.30	0.0 <sup>3</sup>	-78	48.09	7.03	-	-	-    0.946
61.04	0.836	0.66	0.04	-41	-	-	21.61	-	1.026    -
61.06	0.832	0.66	0.04	-37	-	-	20.75	-	1.109    -
49.07	0.831	0.70	0.11	-19	-	-	20.93	-	1.085    -
41.1	0.800	1.55	0.07	-20	-	-	22.80	-	0.931    -
4.12	0.769	1.20	0.0 <sup>3</sup>	-45	48.63	6.75	-	0.05	-    0.963
19.01	0.765	1.24	0.08	-20	50.03	7.50	21.88	-	1.040    1.035
19.07	0.657	1.34	0.08	-21	48.85	6.91	21.15	-	1.065    0.980
19.02	0.649	0.89	0.08	-19	48.65	6.85	-	-	-    0.973
19.05	0.506	3.12	0.05	-20	49.26	6.73	-	-	-    1.000
19.03	0.487	1.70	0.12	-18	48.12	6.94	21.71	-	1.108    0.947
19.04	0.478	1.61	0.02	-18	50.43	7.39	21.62	-	1.025    1.055
3.21	0.312	0.96	0.04	-33	46.79	6.61	-	-	-    0.891
41.2	0.211	6.05	0.08	-20	-	-	22.41	-	0.961    -
41.3	0.203	6.16	0.02	-20	-	-	22.34	-	0.967    -
Average Values					48.77	6.97	21.72		
Standard Deviation					1.08	0.30	0.66		
Calculated Composition (Equimolar Copolymer)					49.29	6.89	21.93		

Remarks: 1. Mole fraction cyclohexene in comonomer mixture

2. Prepared in chloroform

3. "Spontaneous" initiation with as received cyclohexene

copolymer composition demonstrates a probability of only approximately 0.02 that the copolymers are not of equimolar composition. From the low chlorine content of one of the samples it can be inferred that negligible chain transfer to solvent occurs during polymerization.

IIIIf2. Infrared analysis. The infrared absorption spectra of the copolymers were characterized by five major bands. These are attributed to C-H and S-O vibrations as follows: <sup>114</sup>

<u>Band Assignment</u>	<u>Frequency, <math>\text{cm}^{-1}</math></u>
Asymmetric $\text{CH}_2$ stretch	2926
Symmetric $\text{CH}_2$ stretch	2853
$\text{CH}_2$ scissoring	1448
Asymmetric $\text{SO}_2$ stretch	1301
Symmetric $\text{SO}_2$ stretch	1114

No absorption was apparent in the C = C vibration region,  $1650\text{-}1680\text{ cm}^{-1}$ , demonstrating the absence of appreciable cyclohexene monomer or polymer unsaturation. A typical infrared spectrum is presented in Figure 8. As would be expected from the relative constancy of the copolymer elemental analyses, no correlation was found between the sulfur content and the ratios of C-H to S-O absorption peaks. Average values and standard deviations of the absorption peak ratios for the 41 samples tested were found to be:



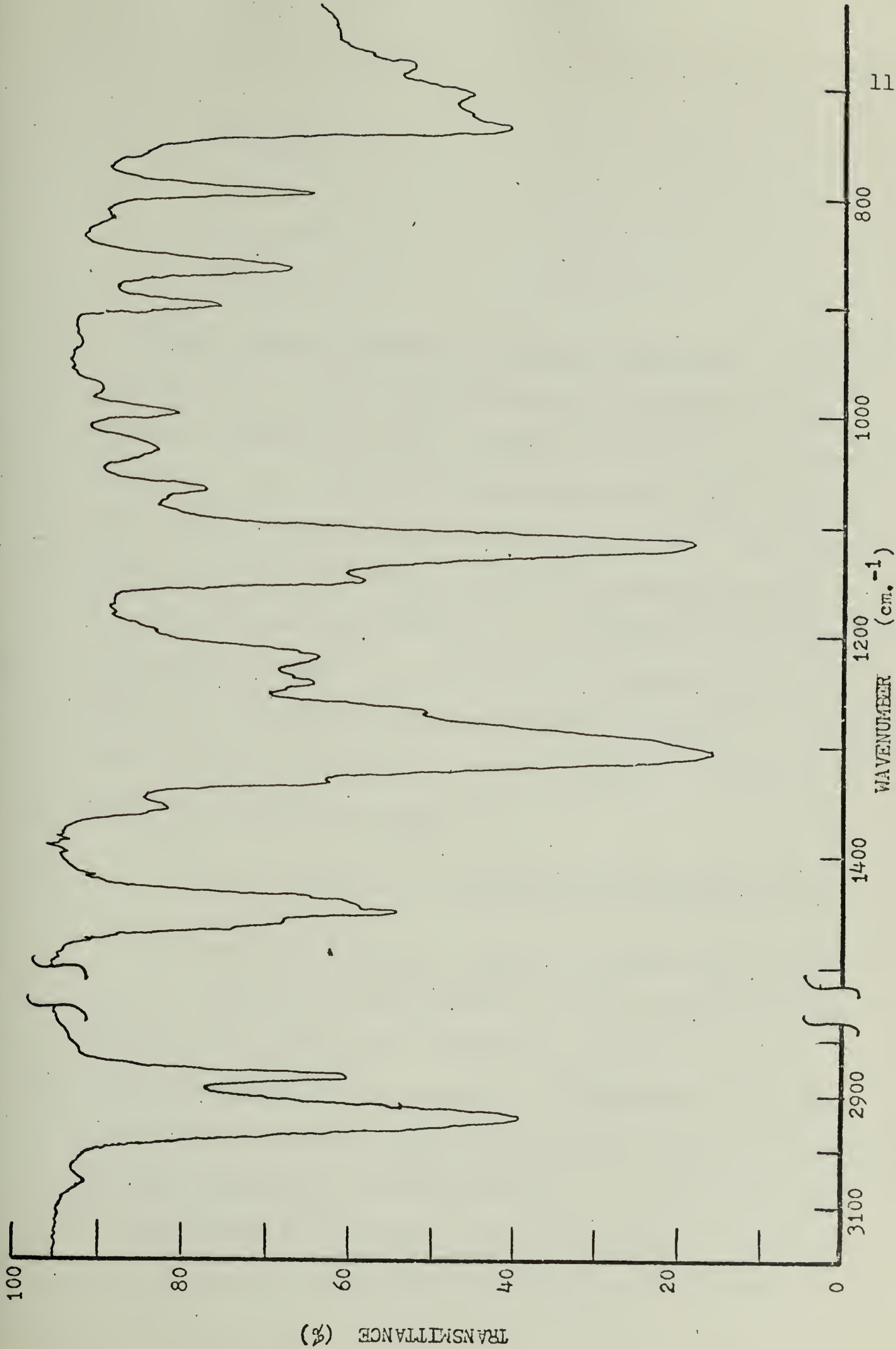


Figure 8. Infrared absorption spectrum of typical poly(cyclohexene sulfone)

$\text{OD}_{2926}/\text{OD}_{1301}$	$0.457 \pm 0.067$
$\text{OD}_{2926}/\text{OD}_{1114}$	$0.489 \pm 0.061$
$\text{OD}_{1448}/\text{OD}_{1301}$	$0.286 \pm 0.074$
$\text{OD}_{1448}/\text{OD}_{1114}$	$0.305 \pm 0.072$

IIIIf3. Nuclear magnetic resonance analysis. The 60 MHz spectrum of the copolymer in  $\text{CDCl}_3$  exhibited three broad resonances at 5.88, 7.76 and 8.18  $\tau$  in the intensity ratio of 1:2:2. This is in agreement with the result of Ivin, Navratil and Walker, who assigned these resonances to the main-chain protons, the  $\alpha$ - $\text{CH}_2$  groups and the  $\beta$ - $\text{CH}_2$  groups respectively.<sup>61</sup> As expected, no difference was evident between the spectra of a copolymer prepared from a 4.0 sulfur dioxide/cyclohexene comonomer ratio and that prepared from a 0.25 comonomer ratio. A typical spectrum is shown in Figure 9.

### IIIg. Preliminary Copolymerization Experiments

To assess the general effect of some of the experimental variables on the kinetics of the copolymerization reaction, two series of experiments were carried out. In these experiments the comonomers, solvents and initiator were placed in serum capped vials and the amount of polymer produced determined gravimetrically. In the first series of experiments no initiator was used, and the yield was determined after reacting for 24 hours. The results of

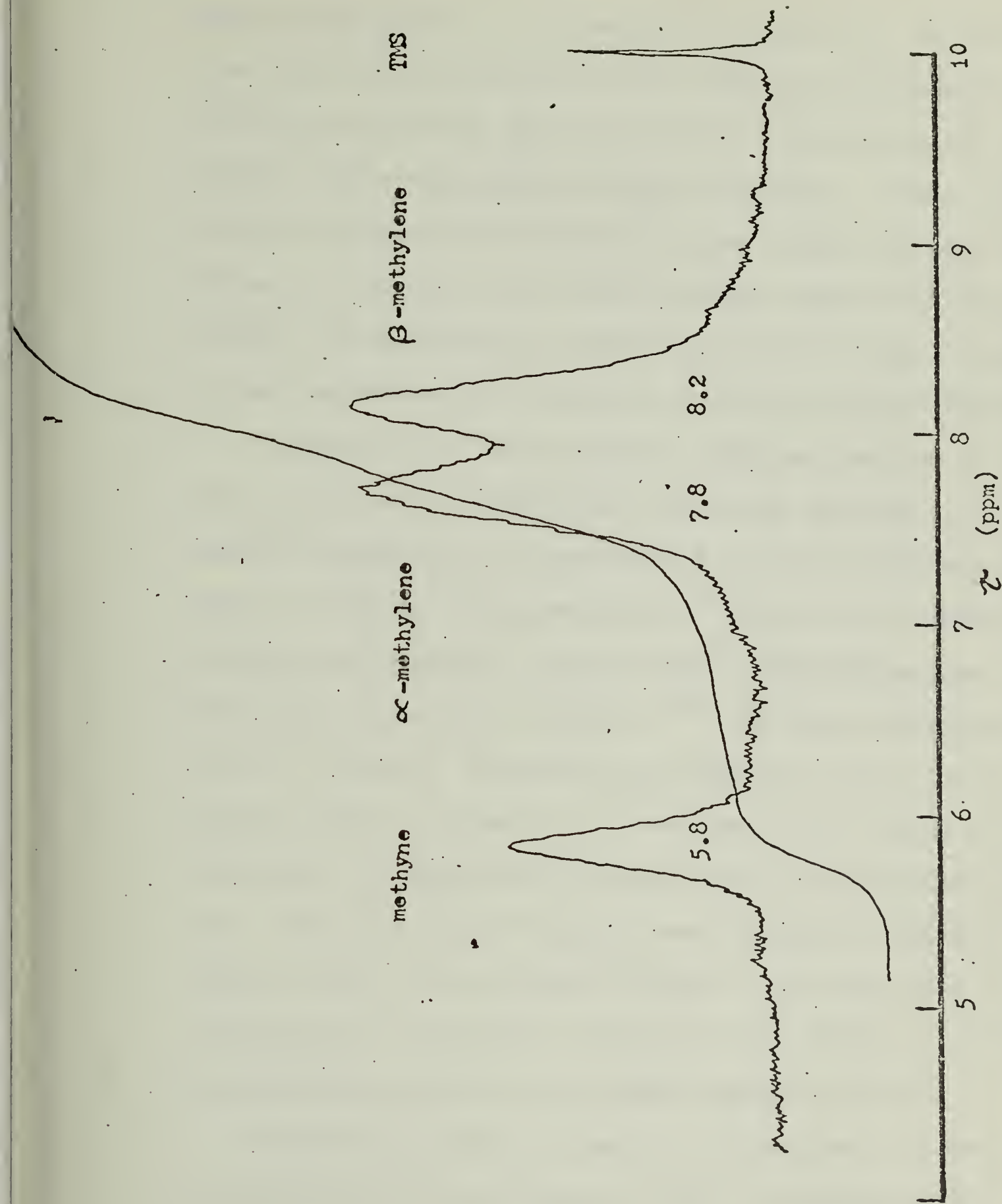


Figure 9. 60 MHz NMR spectrum of typical poly(cyclohexane sulfone) 10 % solution in  $\text{CDCl}_3$ . Spectrum prepared at room temperature



these experiments are presented in Table VI. It is evident from these experiments that the reaction proceeded to significant conversion when unpurified cyclohexene was used without any added polymerization initiator. When this comonomer was purified by distillation under nitrogen from sodium, no polymer was formed without added initiator. Neither the addition of oxygen nor of di-*t*-butyl peroxide in low concentration served to initiate polymerization.

Although the "spontaneous" copolymerization of cyclohexene and sulfur dioxide has not been reported, the above results regarding the spontaneity of this copolymerization tend to confirm the hypothesis of Sartori and Lundberg regarding the reported "spontaneous" copolymerization of norbornene and sulfur dioxide.<sup>85</sup> The data presented in Table VI clearly show that an impurity in the cyclohexene, which is removed by treatment with sodium and distillation, is effective in initiating the copolymerization. The results of Sartori and Lundberg's experiments indicate that the initiator present as an impurity in the cyclohexene is probably a hydroperoxide which is formed by air oxidation of the cyclohexene and/or solvents.

Failure to achieve complete conversion in these experiments can be attributed to the low concentration of initiator present as an impurity in the cyclohexene or to the rapid decomposition of this initiator, discussed in

TABLE VI  
Preliminary Experimentation, Copolymer Yield after 24 Hrs.  
No Initiator Added

Run Ident.	C <sub>6</sub> H <sub>10</sub> Purity	$\frac{[S]_0}{[D]_0}$ mol <sup>2</sup> l <sup>-2</sup>	$\frac{[S]_0}{[D]_0}$	Yield, %	Temp., °C	Solvent
6.2	As Rec'd	26.3	0.28	24.8	-78	Neat
9.1	"	21.5	0.22	32.3	"	"
9.4	"	10.5	0.63	44.6	"	"
6.1	"	61.7	4.1	0.8	"	"
9.2	As Rec'd	8.9	0.19	84.2	-78	CHCl <sub>3</sub>
9.3	"	0.8	0.26	70.6	"	"
13.1	"	0.4	0.27	53.2	"	"
13.2	"	0.1	0.27	34.0	"	"
18.1	As Rec'd	21.7	0.25	25.2	-20	CHCl <sub>3</sub>
18.2	"	6.3	0.26	18.2	"	"
18.3	"	0.2	0.39	0.0	"	"
18.4	"	0.1	0.25	0.0	"	"
37.1	As Rec'd	7.6	0.27	37.0	-78	CH <sub>2</sub> Cl <sub>2</sub>
37.2	"	3.0	0.26	33.3	"	"
37.3	"	0.9	0.26	19.5	"	"
37.4	"	0.6	0.27	14.5	"	"
6.4	Purified <sup>1</sup>	26.3	0.28	0.0	-78	Neat
13.3	"	24.5	0.25	0.0	"	"
13.4 <sup>2</sup>	"	24.7	0.26	0.0	"	"
13.5 <sup>3</sup>	"	24.1	0.25	0.0	"	"
6.3	"	61.7	4.13	0.2	"	"
9.5	"	0.9	0.26	0.0	"	"

1    Refluxed over sodium and distilled

2    0.005 M Di-t-butyl peroxide added

3    0.004 M O<sub>2</sub> added

further detail in sections IIIi and IIIj. The data presented in Table VI also show that higher yield of copolymer was obtained at a low starting ratio of sulfur dioxide to cyclohexene. This result is attributed to greater reactivity of the sulfonyl radical in adding cyclohexene compared to the addition of sulfur dioxide to the cyclohexyl radical. The overall reaction rate is thus increased more by an increase in the cyclohexene concentration. This effect is discussed in greater detail in a subsequent section.

As expected, the yield of copolymer increased with increasing total monomer concentration (approximated by the initial concentration product  $[S]_0 [D]_0$  in Table VI). On the other hand, the tendency toward decreasing yield with increasing value of the product of comonomer concentrations as shown by the data for copolymerizations conducted without solvent, is attributable to variation in the comonomer ratio which, due to the greater density of the sulfur dioxide, results in a higher total monomer concentration (expressed on a volume basis) at a high ratio of sulfur dioxide to cyclohexene.

Copolymerization in chloroform proceeded to a higher yield than reactions conducted in dichloromethane. The reason for this solvent effect is not clear but may be due to a difference in hydroperoxide content of the solvents



used. Yield of polymer obtained in experiments conducted at  $-20^{\circ}\text{C}$  was found to be less than the yield at  $-78^{\circ}\text{C}$  at approximately equal comonomer concentrations. This effect may be due to the increased rate of heterolytic decomposition of initiator at the higher temperature. This reaction competes with polymerization initiation in utilizing hydroperoxide. The effect of temperature on the initiator decomposition reactions and the significance of initiator decomposition in controlling the reaction rate are discussed in detail in a subsequent section.

In an additional series of preliminary experiments, the effects of solvent on polymerization and the yield-vs.-time relationship was investigated using the technique described above. In these experiments, unpurified t-butyl hydroperoxide (approximately 74% assay determined by infrared absorption of the  $3552\text{ cm}^{-1}$  band) was injected into the serum capped vials. The results of these experiments are tabulated in Table VII and in the following summary:

(1) the reaction proceeded to a limiting conversion with a yield significantly less than 100% within approximately one hour;

(2) the limiting conversion reached was affected by both the initiator and total monomer concentration, increasing as both of these variables increased;

(3) conversion was increased significantly when an equivalent amount of initiator was charged in two smaller charges during the reaction rather than in one charge at the start of the reaction;

(4) the apparent equilibrium or limiting yield was affected by the reaction medium.

Appreciably higher yield than that obtained in chlorinated solvents was obtained in acetone and in cyclohexanone, while the polymer yield in methanol and dimethylformamide was found to be significantly lower. No further investigation of the solvent effect was undertaken. Based on the kinetic analysis presented subsequently, it is felt that the solvent affects the initiation rather than the chain propagation reaction.

Qualitative experimentation was carried out to determine which of the commonly used free radical initiators would be effective in the low temperature copolymerization of cyclohexene and sulfur dioxide. When purified cyclohexene monomer was used, polymer was obtained only by the use of t-butyl hydroperoxide or cumene hydroperoxide initiators. No polymerization occurred in experiments in which  $\text{AgNO}_3$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{NaOOC}(\text{CH}_3)_3$ ,  $\text{H}_2\text{O}_2$ , di-t-butyl peroxide or benzoyl peroxide initiators were employed.

TABLE VII

Yield of t-Butyl Hydroperoxide Initiated Copolymerization  
at  $-32^{\circ}\text{C}$  and Equimolar Comonomer Charge Ratio

Run	$\frac{[\text{S}]_0}{[\text{D}]_0}$	$\frac{[\text{S}]_0}{[\text{D}]_0}$	$[\text{I}]_0$	Time, hrs.	Solvent	Solvent	Yield, %
Ident.	$\text{mol l}^{-2}$	$\text{mol l}^{-2}$	$\text{mol l}^{-1}$		1	2	
174.1	8.89	0.91	0.011	0.65	$\text{CH}_2\text{Cl}_2$	none	1.59
174.2	8.05	0.89	0.011	1.05	"	"	2.64
174.3	8.45	0.89	0.011	4.00	"	"	1.88
168.5	7.93	1.00	0.133	1.00	$\text{CH}_2\text{Cl}_2$	none	31.21
174.4	8.02	0.98	0.138	1.00	"	"	36.44
161.1	8.20	0.89	0.114	1.00	"	"	35.62
161.2	8.04	0.94	0.134	2.00	"	"	34.64
161.3	8.16	0.98	0.144	3.38	"	"	31.36
161.4	7.96	0.95	0.129	20.50	"	"	31.96
161.5	7.99	0.95	0.131	27.18	"	"	37.31
171.1	8.57	0.99	0.134	0.65	"	"	28.18
171.2	8.27	0.92	0.131	1.03	"	"	31.90
163.7	8.09	0.92	0.131	2.50	"	"	34.98
174.5	0.135	0.83	0.145	1.00	$\text{CH}_2\text{Cl}_2$	none	18.8
174.6	0.115	1.03	0.160	3.00	"	"	7.5
161.6	47.39	0.92	0.305	2.00	neat	none	47.4 <sup>1</sup>
163.8 <sup>2</sup>	8.08	0.92	0.112	2.50	$\text{CH}_2\text{Cl}_2$	none	45.29
163.1	8.48	0.96	0.130	1.00	Toluene	none	42.73 <sup>1</sup>
163.2	8.56	0.90	0.124	2.50	"	"	48.27 <sup>1</sup>
163.3	9.00	0.90	0.148	1.00	$\text{CHCl}_3$	"	13.79
163.4	8.54	0.95	0.126	2.50	"	"	17.91
163.5	8.64	1.04	0.144	1.00	$\text{C}_6\text{H}_5\text{Cl}$	"	24.52
163.6	8.70	0.94	0.135	2.50	"	"	30.15



TABLE VII  
(Continued)

Run Ident.	$[S]_0 [D]_0$ $\text{mol}^2 \text{l}^{-2}$	$[S]_0 / [D]_0$	$[I]_0$ $\text{mol l}^{-1}$	Time, hrs.	Solvent 1	Solvent 2	Yield, %
168.1	8.65	1.00	0.120	1.00	CH <sub>3</sub> OH	none	0.0
168.2	8.34	1.00	0.132	1.00	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> OH	2.33
168.3	8.11	1.00	0.121	1.00	(CH <sub>3</sub> ) <sub>2</sub> CO	none	43.54
168.4	7.95	1.00	0.137	1.00	CH <sub>2</sub> Cl <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> CO	54.67
171.3	8.06	0.93	0.121	0.53	"	"	44.4
171.4	7.98	0.90	0.155	3.00	"	"	61.9
171.5	8.00	0.93	0.144	1.00	"	"	58.8
171.6	8.71	0.98	0.146	1.00	CHO	none	59.3
171.7	8.26	0.92	0.135	1.00	DMF	"	0.0

## Remarks:

1 Polymer insoluble in medium

2 Two equal charges of t-butyl hydroperoxide during reaction

CHO Cyclohexanone

DMF Dimethylformamide

### IIIh. Copolymer Chain Length

IIIh1. Solvent effect in gel permeation chromatography. The chain length distribution of a given sample was determined both in tetrahydrofuran and in dimethyl formamide containing 0.1 M LiBr. As shown in the tabulation below and in Figure 10, the observed distribution was found to be much broader in tetrahydrofuran because of the later elution of higher chain length residues. This effect causes the chain length averages to appear lower in the less polar solvent, tetrahydrofuran.

#### Solvent Effect on Chain Length Averages of

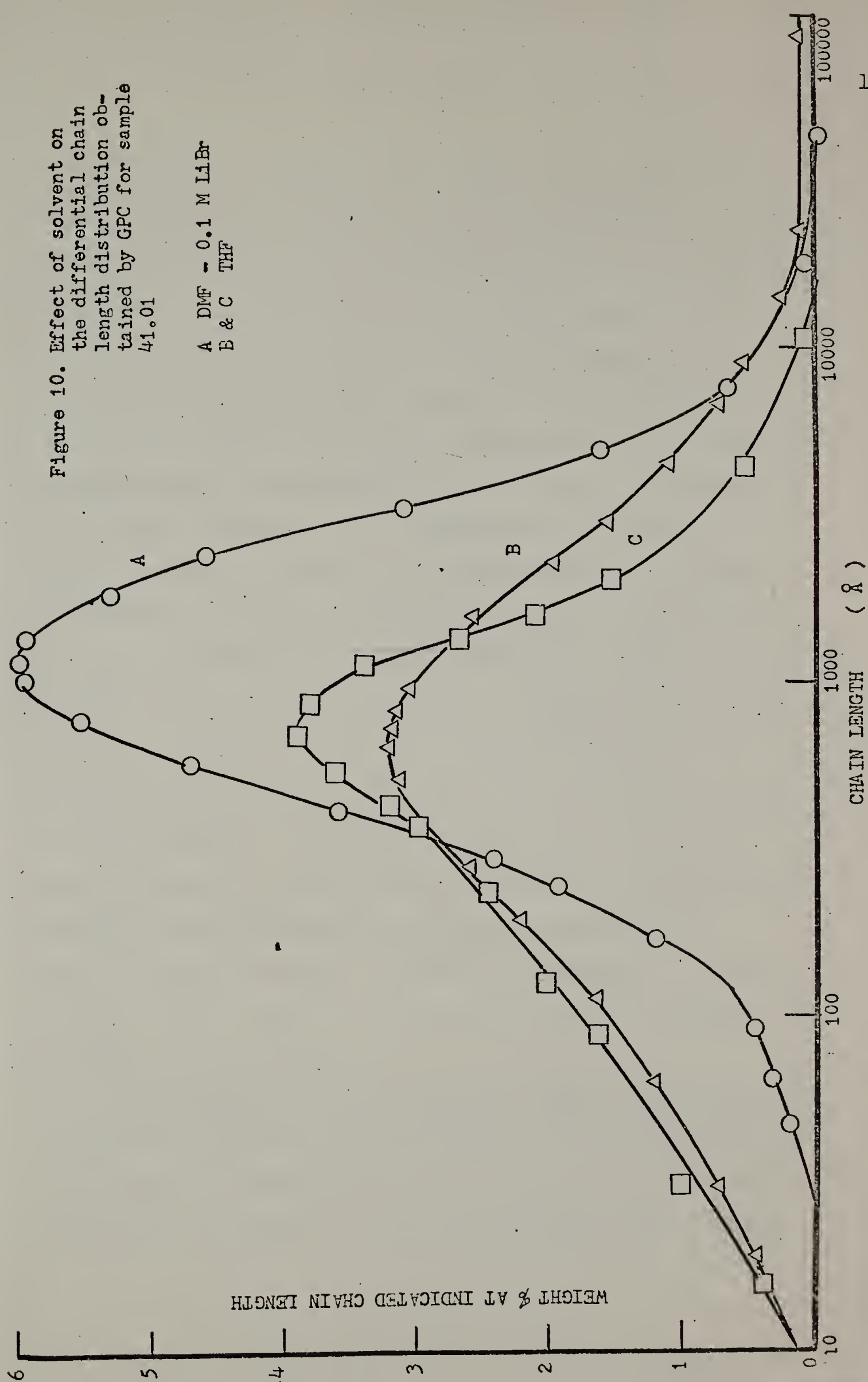
##### Polymer Sample 41.01

<u>Solvent</u>	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$	<u>Curve in Figure 10</u>
DMF- 0.1 M LiBr	578	1730	3.0	A
THF	140	840	6.0	C
THF	149	2330	15.6	B

$\bar{A}_n$  and  $\bar{A}_w$  refer to the number and weight average chain length,  $\text{\AA}$ , respectively. The large spread in the duplicate determinations of  $\bar{A}_w$  in THF is brought about by relatively slight differences in the high molecular weight tail. The solvent effect is attributable to preferential absorption of the higher molecular weight fractions of the relatively polar polysulfone on the column, which can presumably be reduced by covering the adsorbing sites on the column with

Figure 10. Effect of solvent on the differential chain length distribution obtained by GPC for sample 41.01

A DMF - 0.1 M LiBr  
B & C THF





a small amount of salt.<sup>115</sup> It should be pointed out that, although the analyses in the two solvents were performed at the University of Massachusetts and at DeBell and Richardson, the large low molecular weight tail in tetrahydrofuran was observed at both laboratories.

Since facilities for carrying out further analyses were limited to the use of tetrahydrofuran as a solvent, the experimental distributions determined in tetrahydrofuran were corrected for adsorption by calculation. A chain length vs. elution volume calibration curve was constructed from data relating the observed cumulative weight fractions in tetrahydrofuran to the chain lengths these fractions would exhibit if the analysis were performed in the more polar, salt containing solvent. The calibration was based on duplicate runs in both solvents of three samples. The data are presented in Figure 11 and the best fit of the points determined by multivariate linear regression analysis, yielding the equation:

$$\ln A = 6.086 + 0.638C - 0.0258C^2 + 0.000209C^3 \quad (3-11)$$

between chain length, A, and elution count, C, drawn as a curve on the figure.

A comparison of the cumulative weight distributions in the two solvents with determinations in tetrahydrofuran corrected for adsorption effects using this calibration is presented in Figure 12. The number average chain length

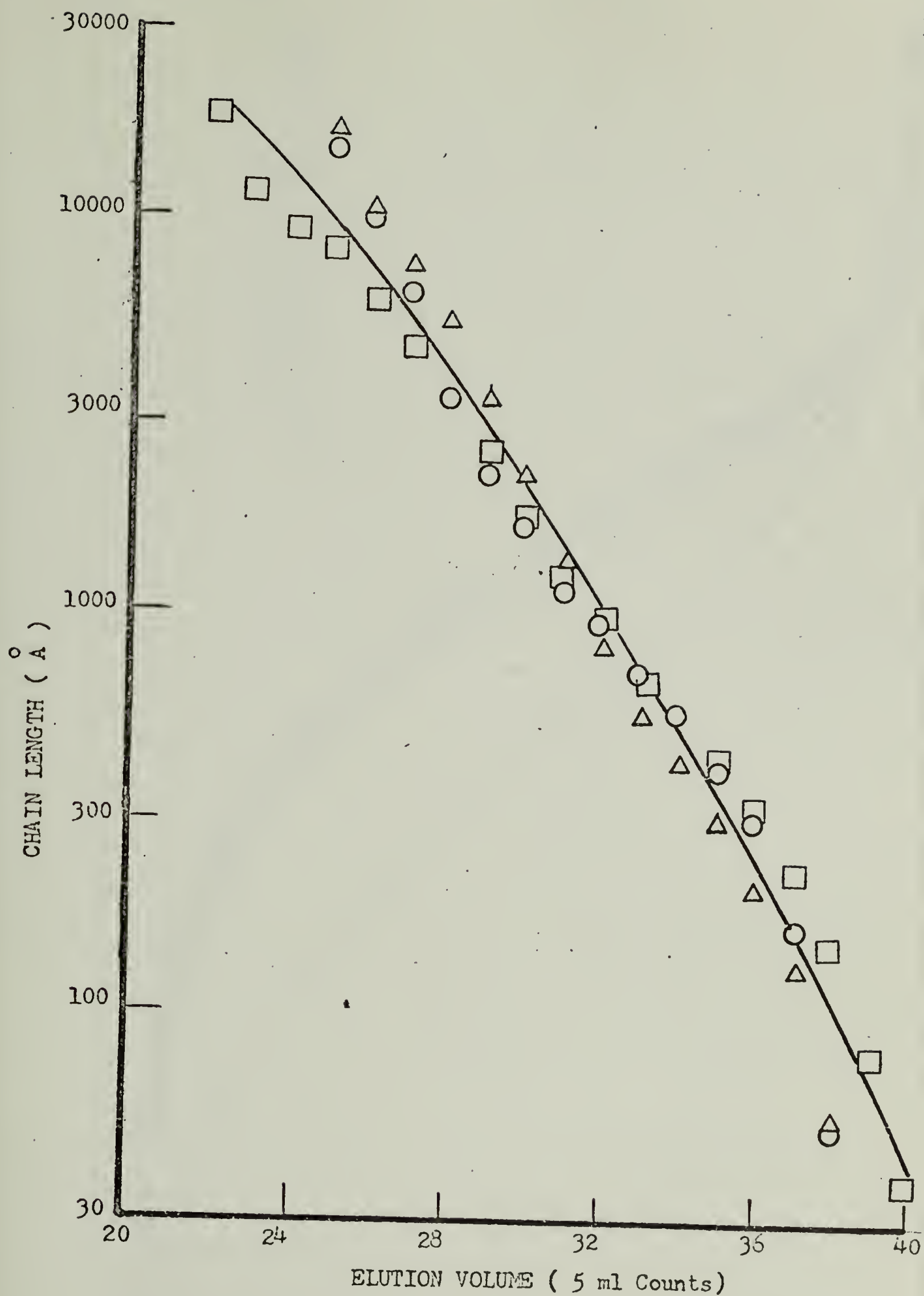


Figure 11. GPC calibration in THF solvent based on chain length determined in DMF- 0.1 M LiEr  
 □ Sample 41.01, ○ Sample 41.02, △ Sample 41.03

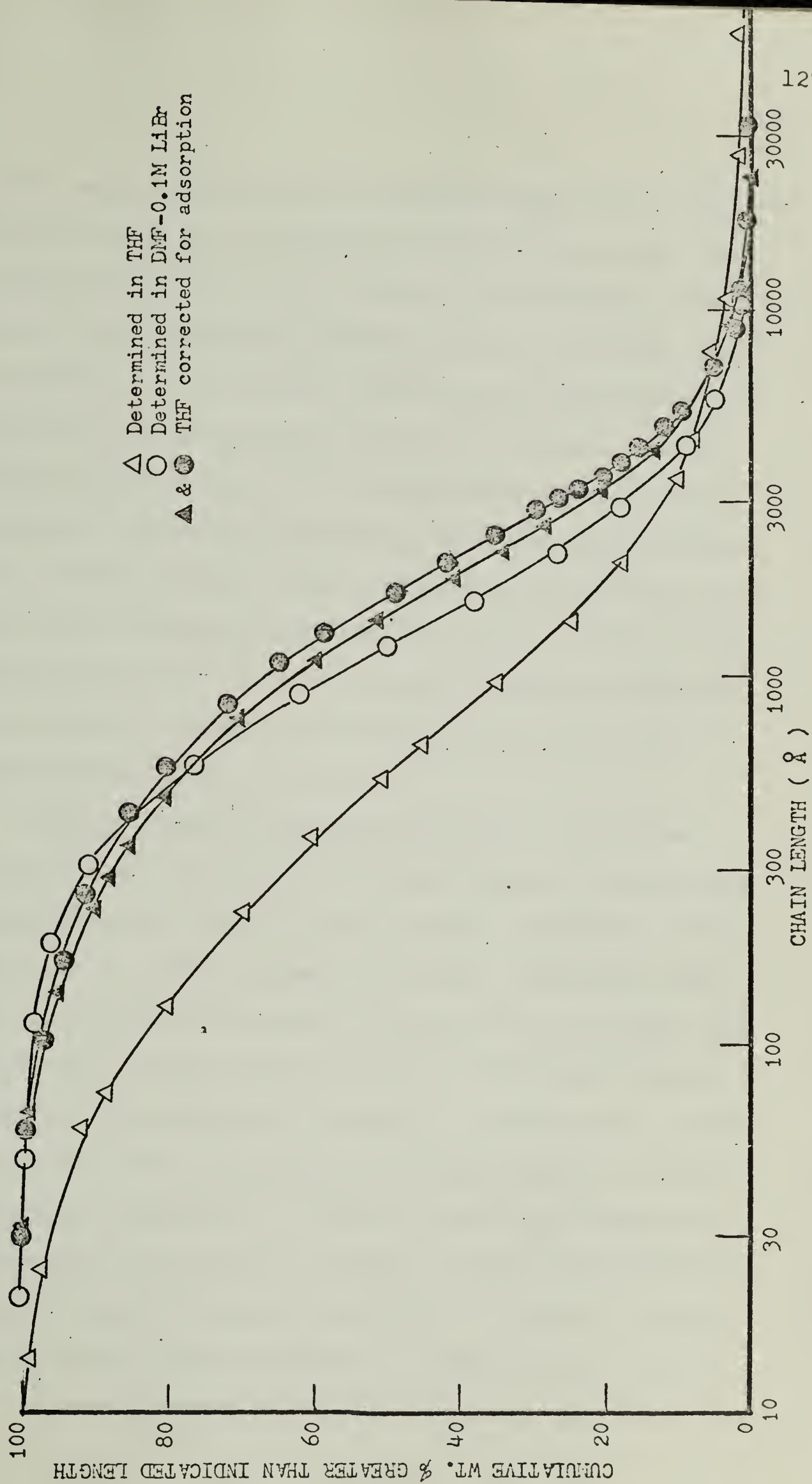


Figure 12. Effect of solvent on the cumulative chain length distribution of sample 41.01 measured by GPC



of the sample determined in tetrahydrofuran corrected for adsorption was calculated to be 591 and 543 in two determinations compared to a value of 578 obtained from the sample run in dimethyl formamide-LiBr. The chain length distribution ratio,  $\bar{A}_w/\bar{A}_n$ , determined in tetrahydrofuran and corrected was found to equal 3.8 and 4.0, somewhat higher than the value of 3.0 found by performing the analysis in dimethyl formamide-LiBr. Subsequent reference to chain lengths and distributions are based on the corrected tetrahydrofuran results, and, although the absolute magnitudes of the values are somewhat imprecise, the corrected values should reflect relative differences between samples fairly.

IIIh2. Length of polymer segment. The number average molecular weight of polymer sample 41.01 was determined to be 11400 by vapor pressure osmometry. The length of a polymer segment (Q value) calculated from the quotient of the number average molecular weight and the number average chain length of this sample determined by GPC was found to equal 20. This value compares with one of 28 calculated from bond lengths of the alternating copolymer.<sup>116</sup> Due to the larger degree of uncertainty of molecular weight (or degree of polymerization) values obtained from the GPC results by using either of the above estimates of the Q value, the GPC

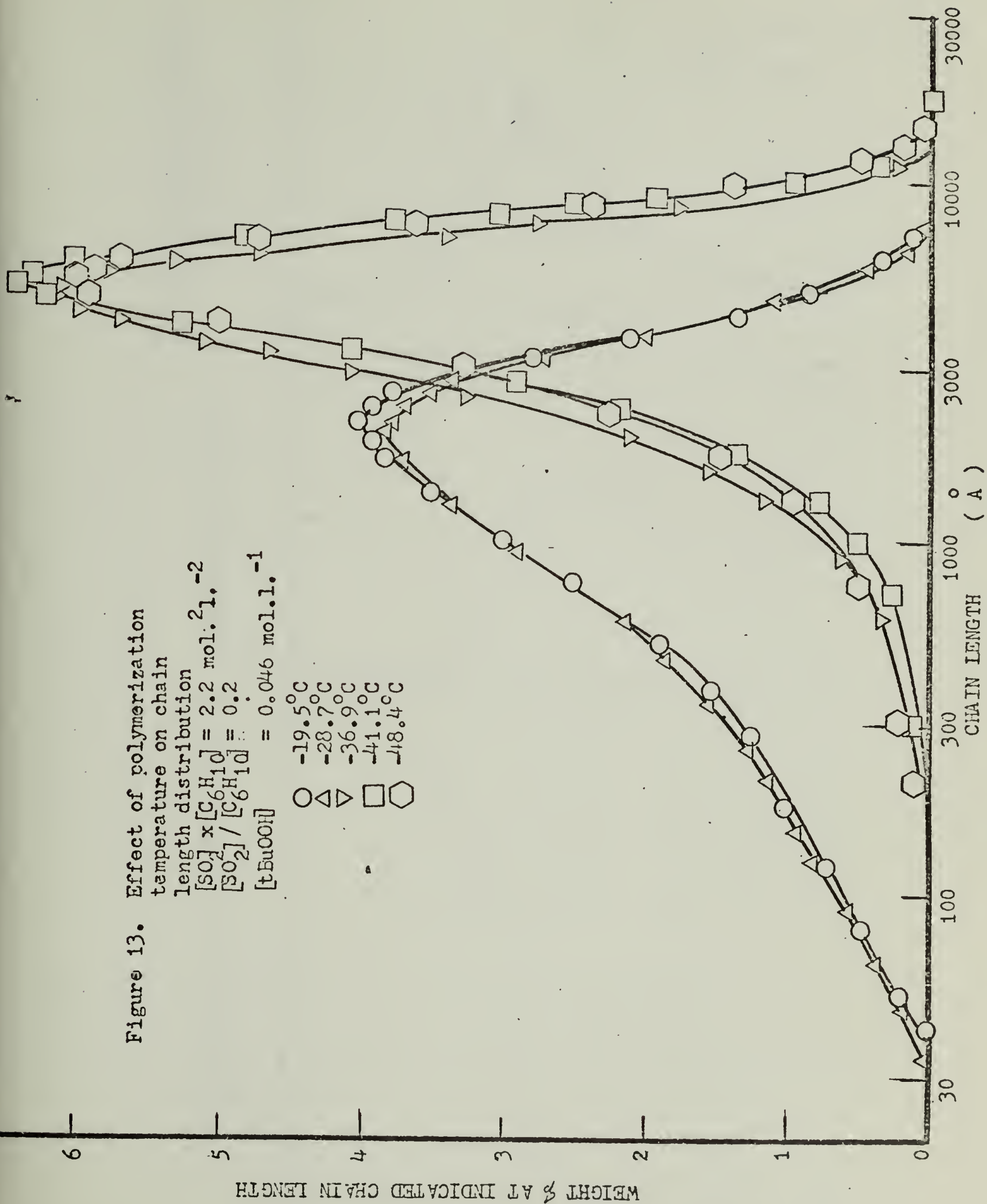
results are reported only in terms of chain length. Conversion of the data to molecular weights by multiplying by the  $Q$  value was not made.

IIIh3. Effect of polymerization temperature. The effect of polymerization temperature on the chain length distribution is presented in Figure 13 and the effect of temperature on the number average chain length, the polydispersity ratio,  $\bar{M}_w/\bar{M}_n$ , and the overall polymerization rate is presented in Figure 14. These figures show that the molecular weight and molecular weight distribution are discontinuous functions of reaction temperature. At temperatures below approximately  $-30^\circ\text{C}$  the molecular weight distribution was found to be fairly narrow,  $\bar{M}_w/\bar{M}_n = 1.6$ , and the number average chain length found to be fairly high,  $\bar{A}_n = 2500$ . No significant change in these values was apparent in experiments conducted between  $-36$  and  $-48^\circ\text{C}$ . Since the value of the polydispersity ratio,  $\bar{M}_w/\bar{M}_n$ , was found to be less than 2, chain termination is attributable to a radical chain combination rather than to a disproportionation mechanism. 117

At polymerization temperatures between  $-20$  and  $-29^\circ\text{C}$  very polydisperse polymer,  $\bar{M}_w/\bar{M}_n = 3$ , was formed due to a significantly greater fraction of small chains in the copolymers compared to those prepared at lower temperatures. The number average chain length of the polymer samples prepared at the higher temperatures was

Figure 13. Effect of polymerization temperature on chain length distribution  
 $[SO_2] \times [C_6H_{10}] = 2.2 \text{ mol. l.}^{-2}$   
 $[SO_2] / [C_6H_{10}] = 0.2$   
 $[tBuOOH] = 0.046 \text{ mol. l.}^{-1}$

○ -19.5°C  
 △ -28.7°C  
 ▽ -36.9°C  
 □ -41.1°C  
 ◇ -48.4°C





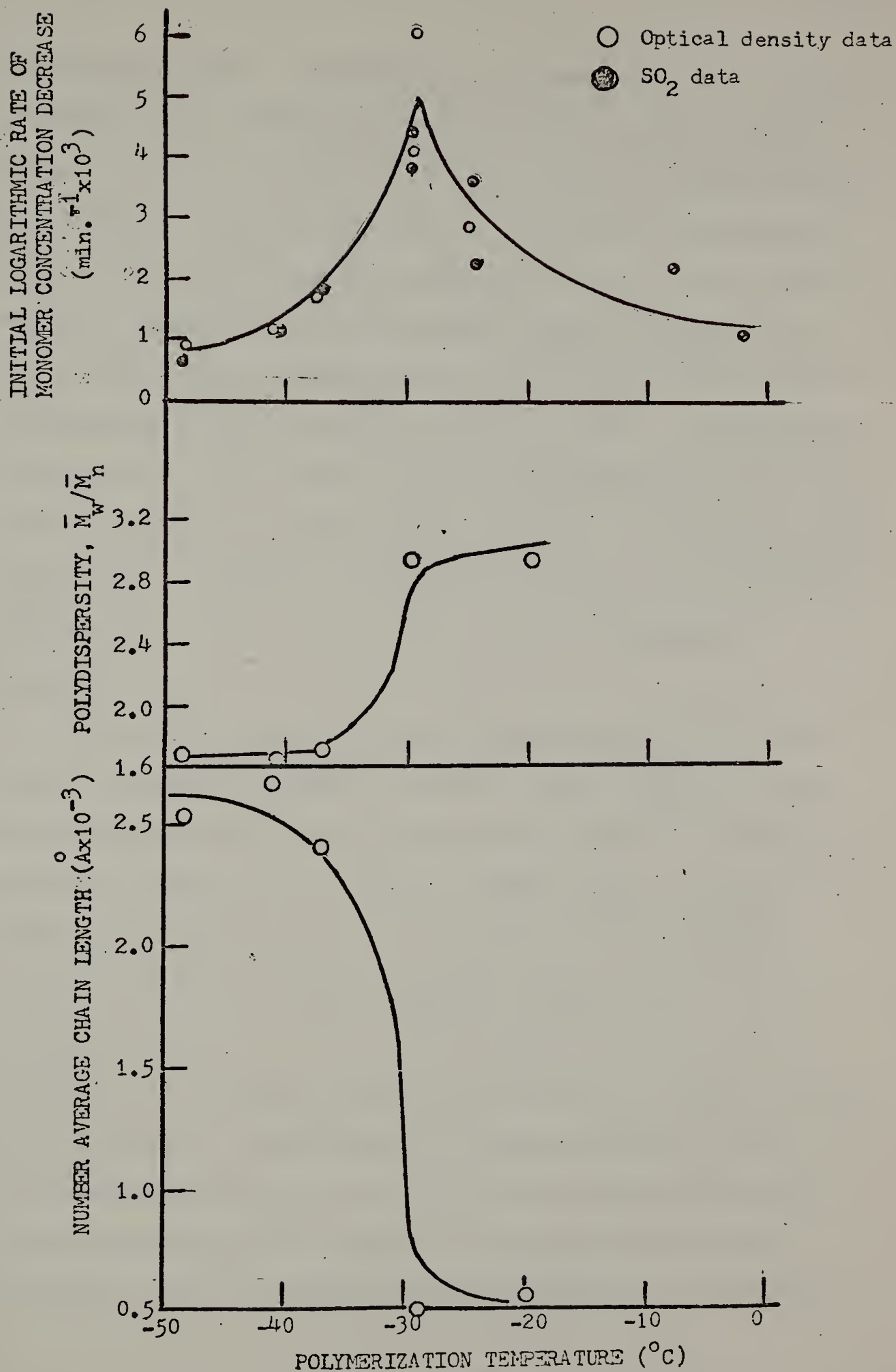


Figure 14. Effect of polymerization temperature on polymer chain length and polymerization rate

approximately 600. No significant change in chain length or chain length distribution was found to occur between  $-20$  and  $-29^{\circ}\text{C}$ . The data thus indicates that the number of short chains remained substantially constant as the reaction temperature was increased from  $-48$  to  $-36^{\circ}\text{C}$ , increased abruptly as the temperature was increased from  $-36$  to  $-29^{\circ}\text{C}$ , and remained at constant high level in the temperature interval between  $-29$  and  $-20^{\circ}\text{C}$ . As indicated in Figure 14, the overall rate of polymerization attained a maximum value at approximately  $-29^{\circ}\text{C}$ . The reaction rate constant vs. reciprocal absolute temperature relationship presented in Figure 29, however, does not exhibit a maximum.

The reversibility of the copolymerization of cyclohexene and sulfur dioxide has been well established and was investigated by Cook, Dainton and Ivin.<sup>93</sup> The fact that the reaction is reversible leads to the ceiling temperature phenomenon, the existence of a temperature where the rate of chain propagation equals the rate of depropagation (i.e., the overall rate of polymerization equals zero) and above which high molecular weight polymer is not formed. Estimating the standard entropy change of the copolymerization to be  $-66.55$  e.u., from the average value determined for a number of alkene-sulfur dioxide reactions, Cook, Dainton and Ivin calculated the enthalpy

change of the copolymerization to be  $-17.8$  kcal/mole measuring the ceiling temperature of mixtures of the undiluted monomers. The equilibrium comonomer concentration product,  $[S]_e [D]_e$ , i.e., the monomer concentration at which the overall polymerization rate equals zero and at which no high molecular weight polymer is formed, is plotted as a function of polymerization temperature in Figure 15 using the thermodynamic constants determined by Cook, Dainton and Ivin and equation (3-12):

$$[S]_e [D]_e = \exp(\Delta H_p/RT - \Delta S_p^0/R) \quad (3-12)$$

Points plotted on Figure 15 represent the final comonomer concentration product (calculated from the measured final sulfur dioxide concentration and the initial and final cyclohexene concentrations) in the experiments for which samples were obtained of the final product for the determination of polymer chain length. The initial comonomer concentration products as well as the majority of the estimated final comonomer concentration products at  $-19^\circ\text{C}$  are in excess of the calculated equilibrium concentrations. These observations, as well as the fact that finite polymerization rates were observed at temperatures above  $-30^\circ\text{C}$ , lead to the conclusion that the decrease in molecular weight occurring at  $-30^\circ\text{C}$  is not attributable to the ceiling temperature phenomenon in



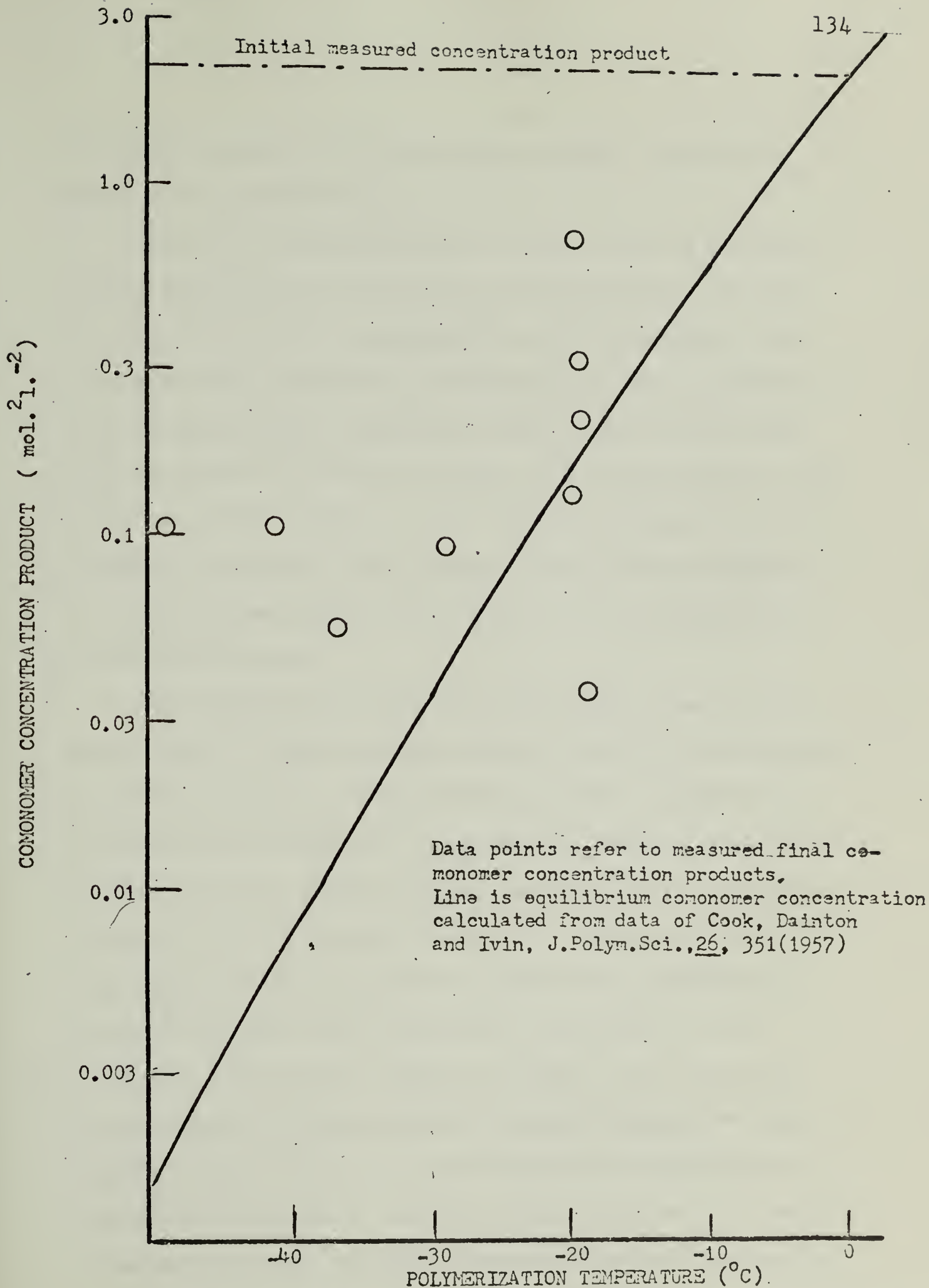


Figure 15. Effect of polymerization temperature on the observed and equilibrium comonomer concentrations

which depropagation of the active polymer chains competes with propagation.

Based on the observation that the rate of polymerization decreased at the end of the experiments and that the final comonomer concentration was calculated to be less than the equilibrium concentration, it is possible that an equilibrium comonomer concentration might have been attained at the end of some of the runs made at temperatures above  $-30^{\circ}\text{C}$ . A more likely explanation for the observed decrease in the reaction rate, which involves the rapid decomposition of initiator, is discussed in a subsequent section.

Nevertheless, the ability of a model based on the occurrence of some depropagation to rectify data relating the initial rate of polymerization to the reciprocal of the absolute temperature (Figure 29), leads to the conclusion that the depropagation reaction plays a significant part in the reaction kinetics. The occurrence of depropagation should lead to a continuous decrease in molecular weight with increasing temperature if the monomer concentration remains constant. The observed discontinuity in the molecular weight temperature relationship may, however, be attributable to depropagation because the molecular weights were determined for samples prepared while the monomer concentration was continually

decreasing. The effect of depropagation on the molecular weight and molecular weight distribution is accentuated by the decreasing monomer concentration occurring during the preparation of the sample. Above the temperature at which a maximum in the polymerization rate-temperature relationship occurs, depropagation plays a significant part in polymer formation. At these higher temperatures, polymer prepared at the end of the reaction will be of significantly lower molecular weight, due to the lower monomer concentration, than that prepared at the beginning of the reaction. The effect of increasing temperature in decreasing molecular weight is thus accentuated by the increased depropagation brought about by the decreasing monomer concentration at the higher temperature. At temperatures below the occurrence of the maximum rate, depropagation plays a relatively minor role and polymer prepared over the whole course of the reaction will be much more homodisperse. The large, discontinuous effect of temperature on molecular weight may, thus, be attributable to the combined effect of depropagation and decreasing monomer concentration during the reaction.

IIIh4. Effect of initiator concentration. The average chain lengths of copolymers prepared keeping all conditions except the t-butyl hydroperoxide concentration constant are given in Table VIII. The chain length



distributions of these copolymers are presented in Figure 16. The general trend of increasing chain length with decreasing initiator concentration is evident. The number average chain length was found to be proportional to the inverse 0.3 power of the initiator concentration rather than the inverse 0.5 power to be expected from normal free radical initiated polymerizations. Additionally, the extreme broadness of the chain length distribution at the lowest initiator concentration is of note.

The generally high polydispersity at  $-19^{\circ}\text{C}$  is ascribed to the participation of the depropagation reaction. The lower than the expected reciprocal 0.5 power dependence of the number average chain length on initiator concentration is attributed to the fact that the *t*-butyl hydroperoxide initiator decomposes by competing homolytic and acid-catalyzed heterolytic mechanisms.<sup>82</sup> The effective initiator concentration is not directly proportional to the concentration of *t*-butyl hydroperoxide because decomposition of the hydroperoxide by the non-radical producing heterolytic decomposition reaction is increased at high hydroperoxide concentrations. The extremely broad distribution of the polymeric product of the experiment conducted at the lowest initiator concentration is attributable to the increased chain length of polymer formed at low initiator

TABLE VIII

Effect of Initiator Concentration on Chain Length Averages

$[I]_0$ , mol/l	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$
0.012	796	4790	6.0
0.023	799	2160	2.7
0.045	560	1670	3.0
0.116	494	1310	2.6

Polymerization temperature:  $-19^\circ\text{C}$ 

$$[S]_0/[D]_0 = 0.20$$

$$[S]_0[D]_0 = 2.2 \text{ moles}^2/\text{liter}^2$$

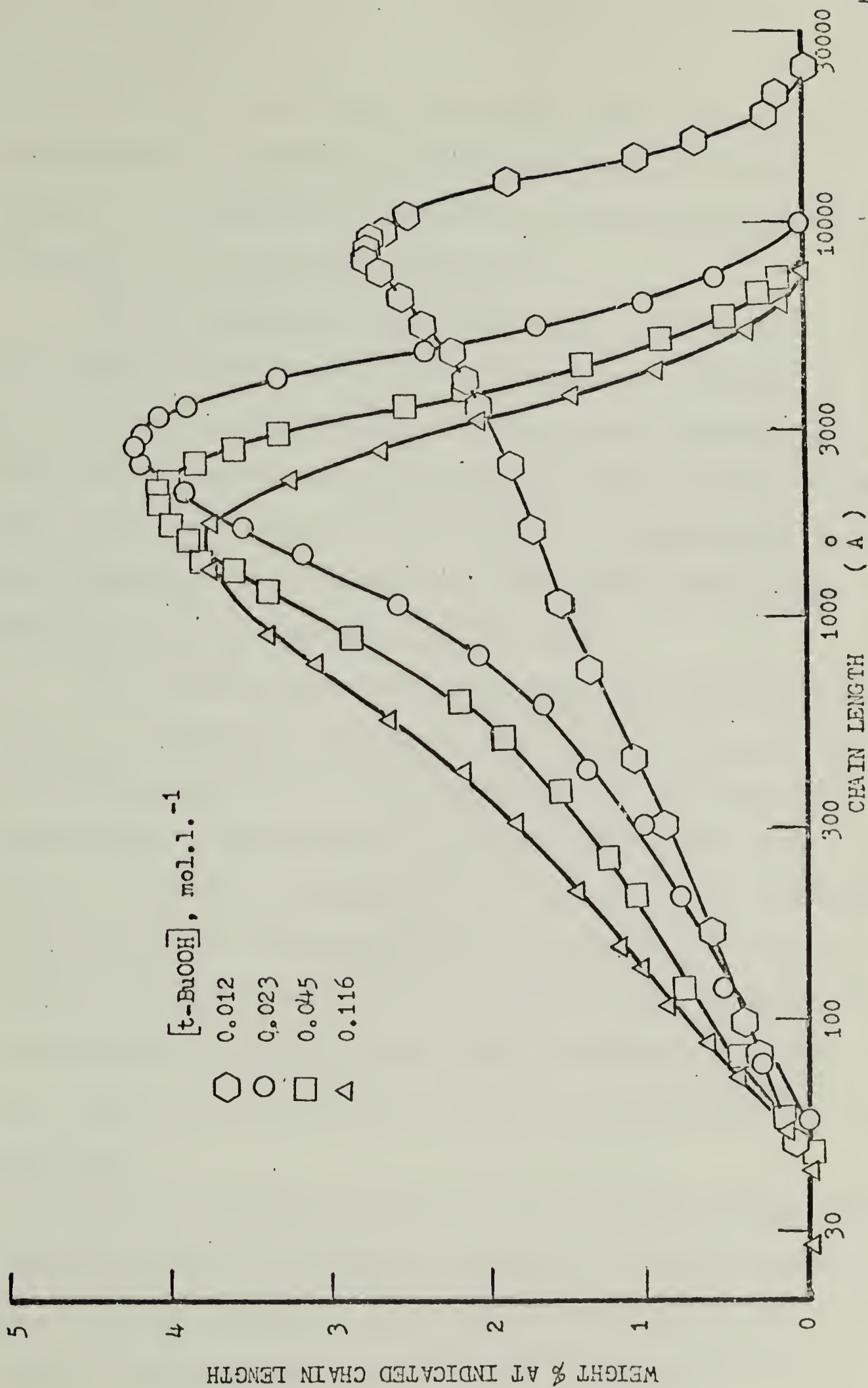


Figure 16. Effect of initial initiator concentration on chain length distribution  
 $[\text{SO}_2] \times [\text{C}_6\text{H}_{10}] = 2.2 \text{ mol.l.}^{-2}$ ;  $[\text{SO}_2] / [\text{C}_6\text{H}_{10}] = 0.2$ ; Temperature =  $19^\circ\text{C}$



concentration as well as to the fact that this reaction was allowed to proceed for twice the normal 60-70 min. period, increasing the variation in effective initiator concentration during the experiment.

IIIh5. Effect of comonomer ratio. An increase in the ratio of sulfur dioxide to cyclohexene resulted in increasing the chain length of the polymer without significant effect on the distribution (Figure 17 and Table IX). Increasing the sulfur dioxide to cyclohexene ratio also resulted in decreasing the observed overall polymerization rate (see sect. IIIi4 (a)).

The kinetic chain length in radical polymerization, (i.e., the degree of polymerization,  $\bar{P}$ , in the absence of chain transfer), is defined as the ratio of the rate of monomer disappearance to the rate of radical formation. From this definition it is evident that a decrease in the rate of polymerization,  $R_p$ , coupled with an increase in chain length with increasing sulfur dioxide concentration implies that the rate of radical formation,  $R_i$ , decreases as the sulfur dioxide concentration is increased.

If the radical forming reaction between sulfur dioxide and t-butyl hydroperoxide is considered to be a second order reaction, increasing the sulfur dioxide concentration should increase the rate of radical formation thereby

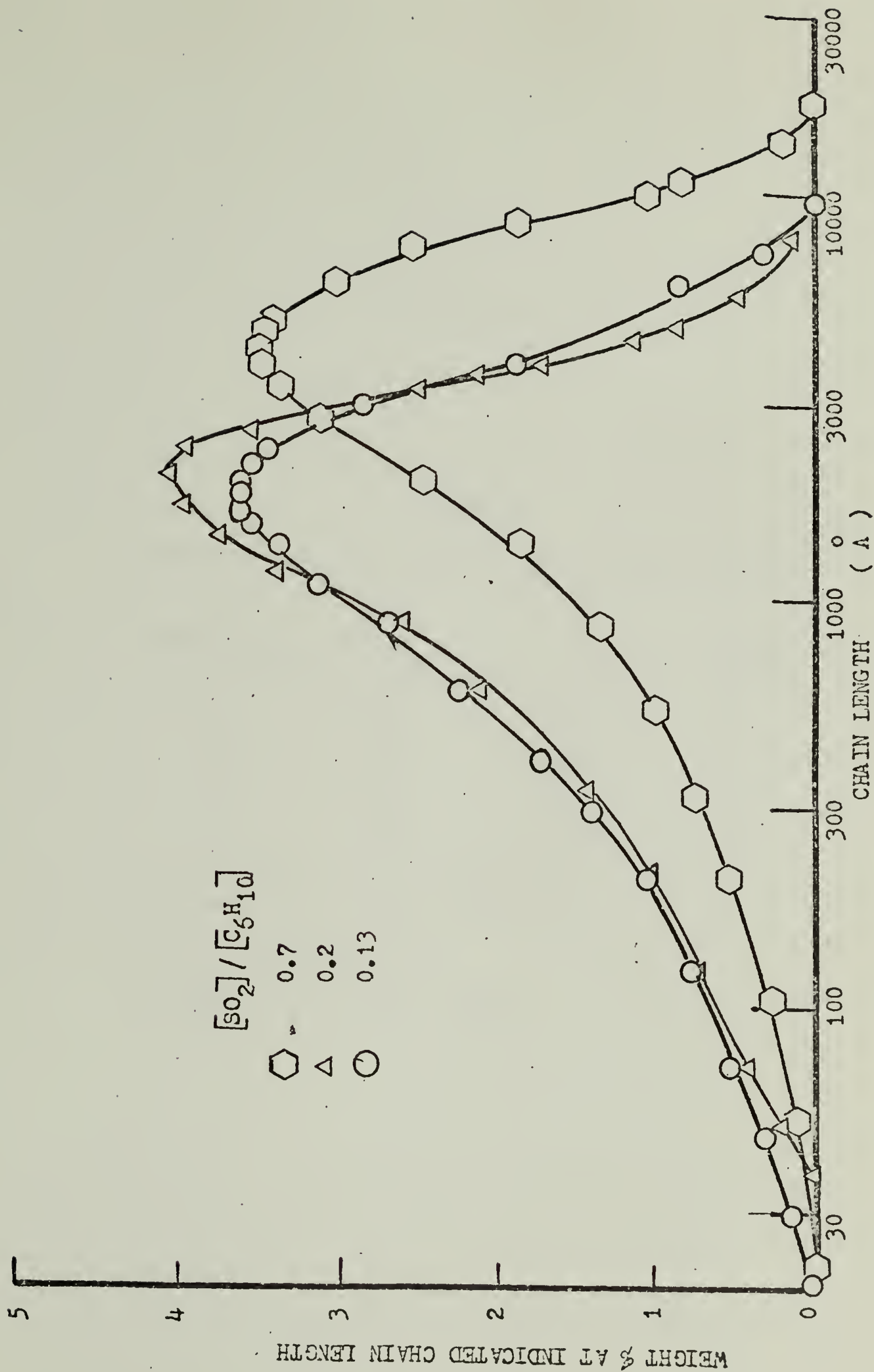


Figure 17. Effect of initial ratio of sulfur dioxide to cyclohexene on chain length distribution  
 $[SO_2] \times [C_6H_{10}] = 2.2 \text{ mol. l}^{-2}$ ;  $[t\text{-BuOOH}] = 0.045 \text{ mol. l}^{-1}$ ;  
 Temperature =  $19^\circ\text{C}$

TABLE IX

Effect of Comonomer Ratio on Chain Length Averages

$[S]_0/[D]_0$	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$
0.70	910	3760	4.1
0.20	560	1670	3.0
0.13	460	1610	3.5

Polymerization temperature:  $-19^{\circ}\text{C}$  $[I]_0 = 0.045$  moles/liter $[S]_0[D]_0 = 2.2$  moles<sup>2</sup>/ liter<sup>2</sup>



increasing the ratio of  $R_p/\bar{P}$ . The observed results are contrary to this hypothesis. From the observations of Flockhart et al. it can be inferred that increasing the sulfur dioxide concentration would have the effect of increasing the concentration of the less reactive of the two radicals formed from the homolytic decomposition of t-butyl hydroperoxide.<sup>81</sup> Since this would decrease the polymer chain length, an increase in primary radical termination cannot account for the observed phenomenon.

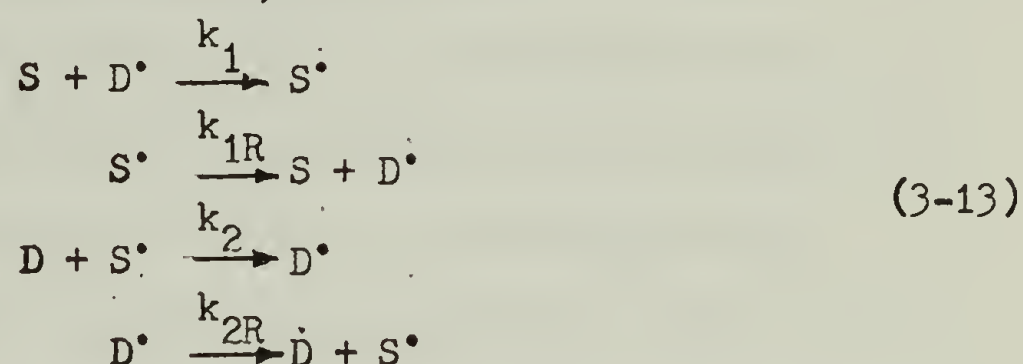
A possible explanation of the observation lies in the effect of sulfur dioxide in increasing the tendency toward heterolytic cleavage and wastage of hydroperoxides reported by Chien and Boss.<sup>82</sup> The di-t-butyl peroxide produced by this reaction decomposes very slowly at the temperatures used, effectively reducing the radical concentration with increasing sulfur dioxide concentration.

### IIIi. Polymerization Reaction Kinetics

#### IIIil. Derivation of Equations

IIIil(a). Propagation by alternating addition. Because sulfur dioxide is incapable of forming a homopolymer and the homopolymerization of cyclohexene has only been achieved at high pressure,<sup>118</sup> only the two crosspropagation reactions need be considered for the copolymerization of these monomers if classical alternating

addition of free monomer molecules to the growing chain is assumed. Since the ceiling temperatures of this type of polymerization are generally observed to be low, the reverse or depolymerization reactions may be of appreciable importance. The four possible reactions occurring during chain propagation, therefore, are:



where S represents sulfur dioxide, D is cyclohexene and  $S^\bullet$  and  $D^\bullet$  are the two types of radical chain end groups present in the reaction. The reactions describing the rates of change of concentration of each of the species are:

$$\begin{aligned}
 -d[S]/dt &= k_1[S][D^\bullet] - k_{1R}[S^\bullet] \\
 -d[D]/dt &= k_2[D][S^\bullet] - k_{2R}[D^\bullet] \\
 d[S^\bullet]/dt &= k_1[S][D^\bullet] + k_{2R}[D^\bullet] - k_{1R}[S^\bullet] - k_2[D][S^\bullet] \\
 d[D^\bullet]/dt &= k_{1R}[S^\bullet] + k_2[D][S^\bullet] - k_1[S][D^\bullet] - k_{2R}[D^\bullet]
 \end{aligned}
 \tag{3-14}$$

If a stationary state concentration of both types of radicals is assumed:

$$d[S^\bullet]/dt = d[D^\bullet]/dt \tag{3-15}$$

then:

$$[D^\bullet] = [S^\bullet] (k_{1R} + k_2[D]) / (k_{2R} + k_1[S]) \tag{3-16}$$

Although the polymerization reaction was found not to proceed at steady state because the rapid decomposition of initiator led to a diminution of reaction rate prior to the exhaustion of the monomers, the steady-state assumption with respect to radical concentrations is applicable. This assumption applies because the radical lifetimes (estimated to be  $90 \text{ ms}^{80}$ ) are much less than the time required (minutes) for a significant decrease in initiator concentration to occur by decomposition.

Using the steady-state approximation, the rates of decrease of comonomer concentrations may be expressed in terms of one of the radical concentrations:

$$-\frac{d[S]}{dt} = -\frac{d[D]}{dt} = [S\cdot] \left( \frac{k_1 k_2 [S] [D] - k_{1R} k_{2R}}{k_{2R} + k_1 [S]} \right) \quad (3-17)$$

The copolymer composition ratio,  $d[S] / d[D]$ , equals unity, (i.e., the copolymer is equimolar) at all comonomer concentrations if only crosspropagation reactions occur in this type of alternating, reversible copolymerization. Since the rates of monomer disappearance are first order in monomer as a rough approximation, it is desirable to calculate the logarithmic rates of the experimentally observed concentration changes,  $-d \ln [M] / dt = -d[M] / [M] dt$ , to facilitate comparison of observed rates with theoretical ones. In terms of the sulfonyl



radical and the comonomer concentrations, the logarithmic rates of sulfur dioxide and cyclohexene concentration changes are:

$$\begin{aligned} -\frac{d\ln[S]}{dt} &= ([S] (k_1 k_2 [S] [D] - k_{1R} k_{2R})) / ([S] (k_{2R} + k_1 [S])) \\ -\frac{d\ln[D]}{dt} &= ([S] (k_1 k_2 [S] [D] - k_{1R} k_{2R})) / ([D] (k_{2R} + k_1 [S])) \end{aligned} \quad (3-18)$$

The concentration of equimolar charge-transfer complex is related to the comonomer concentrations by the equilibrium relationship:

$$K_c = [X] / (([S] - [X]) ([D] - [X])) \quad (3-19)$$

where  $[X]$  is the charge-transfer complex concentration and  $K_c$  is the charge-transfer complex equilibrium constant. For reactions in which association to the complex is slight, as in the case of the sulfur dioxide-cyclohexene complex, the charge-transfer complex concentration is very much less than the concentration of either of the two components and, therefore:

$$[X] = K_c [S] [D] \quad (3-20)$$

Assuming the proportionality of optical density, OD, to charge-transfer complex concentration (i.e., applicability of Beer's law), the optical density attributable to the presence of charge-transfer complex is related to the comonomer concentrations by the following equation:

$$OD = \epsilon_c K_c [S] [D] \quad (3-21)$$

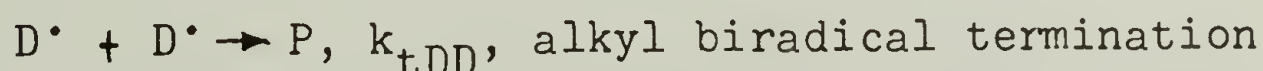
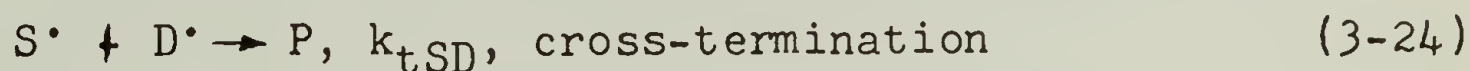
where  $\epsilon_c$  is the extinction coefficient of the charge-transfer complex for a one cm optical path length. The rate of change of the logarithm of optical density is related to the rates of concentration change of the comonomers by equation (3-22), obtained by dividing the first derivative of equation (3-21) by equation (3-21):

$$\frac{d \ln OD}{dt} = \frac{d \ln S}{dt} + \frac{d \ln D}{dt} \quad (3-22)$$

In terms of comonomer and sulfonyl radical concentrations this may be written as :

$$-\frac{d \ln OD}{dt} = [S\cdot] \left( \frac{1}{[S]} + \frac{1}{[D]} \right) \left( \frac{k_1 k_2 [S] [D] - k_{1R} k_{2R}}{k_{2R} + k_1 [S]} \right) \quad (3-23)$$

IIIil(b). Termination with propagation by alternating addition. Bimolecular termination of the radicals may occur by the collision of two macroradicals of like character or two macroradicals of unlike character:



where P represents the terminated polymer. The rate of radical termination is given by the relationship:

$$R_t = 2( k_{tSS} [S\cdot]^2 + k_{tSD} [S\cdot][D\cdot] + k_{tDD} [D\cdot]^2 ) \quad (3-25)$$

If the increase in radical concentration at any time,  $R_i$ , is assumed to be compensated for by a decrease in the radical concentration by radical termination reactions,

$R_t$ , a steady-state concentration of radicals, defined by the equation  $R_i = R_t$ , exists. Using the equation relating the concentrations of the two types of radicals to each other, the sulfonyl radical concentration may be expressed as a function of the initiation rate and the comonomer concentrations by equation (3-26):

$$[S\cdot] = \sqrt{R_i / \left[ 2k_{tSS} + 2k_{tSD} \left( \frac{k_{1R} + k_2[D]}{k_{2R} + k_1[S]} \right) + 2k_{tDD} \left( \frac{k_{1R} + k_2[D]}{k_{2R} + k_1[S]} \right)^2 \right]} \quad (3-26)$$

If it is assumed that termination by one of the three possible mechanisms predominates, the rate of decrease of the logarithm of the charge-transfer complex optical density for conversion to copolymer during the period when the logarithm of the optical density decreases linearly with time is given by the following equations for:

(1) alkyl biradical termination: (3-27)

$$-\frac{d \ln OD}{dt} = \left( \frac{R_i}{2k_{tDD}} \right)^{\frac{1}{2}} \left( \frac{1}{[S]} + \frac{1}{[D]} \right) \left( \frac{k_1 k_2 [S][D] - k_{1R} k_{2R}}{k_{1R} + k_2 [D]} \right)$$

(2) cross-termination: (3-28)

$$-\frac{d \ln OD}{dt} = \left( \frac{R_i}{2k_{tSD}} \right)^{\frac{1}{2}} \left( \frac{1}{[S]} + \frac{1}{[D]} \right) \left( \sqrt{\frac{k_1 k_2 [S][D] - k_{1R} k_{2R}}{(k_{1R} + k_2 [D])(k_{2R} + k_1 [S])}} \right)$$

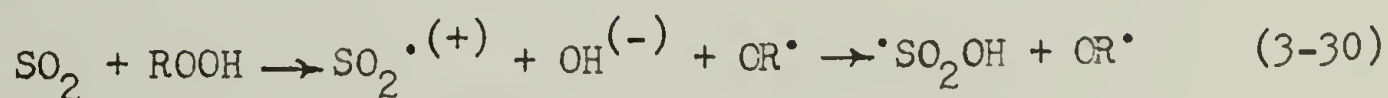


(3) sulfonyl biradical termination: (3-29)

$$-\frac{d\ln OD}{dt} = \left( \frac{R_i}{2k_{tSS}} \right)^{\frac{1}{2}} \left( \frac{1}{[S]} + \frac{1}{[D]} \right) \left( \frac{k_1 k_2 [S][D] - k_{1R} k_{2R}}{k_{2R} + k_1 [S]} \right)$$

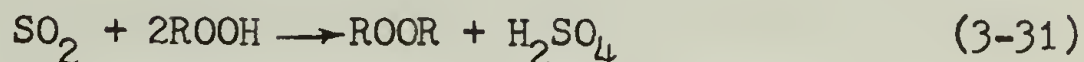
The product of the two depropagation rate constants,  $k_{1R} k_{2R}$ , may be replaced by its equivalent,  $k_1 k_2 [S]_e [D]_e$ . This relationship is obtained by equating the rate of monomer decrease to zero under equilibrium conditions, i.e., when the rate of propagation equals the rate of depropagation and the comonomer concentrations equal  $[S]_e$  and  $[D]_e$ . This transformation permits evaluation of experimental data according to the above equations using the enthalpy and entropy of polymerization data published by Cook, Dainton and Ivin.<sup>93</sup>

IIIil(c). Initiation. The formation of free radicals by the decomposition of hydroperoxides in the presence of sulfur dioxide and an olefin monomer which will copolymerize with the sulfur dioxide is influenced by two factors which profoundly affect the reaction kinetics. Firstly, the rate of homolytic decomposition of the hydroperoxide is increased significantly by a one electron interchange (redox reaction) with the sulfur dioxide.<sup>80,81</sup>



Secondly, and at the same time, a competitive acid-catalyzed heterolytic decomposition of the hydroperoxide

occurs which leads to the formation of dialkyl peroxide.<sup>82</sup>

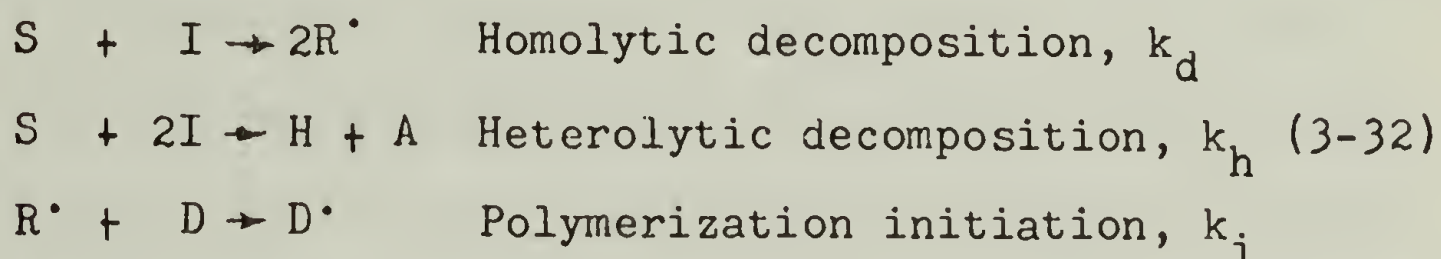


The latter product does not readily take part in an electron interchange reaction with the sulfur dioxide, thus effectively reducing the concentration of active initiator. Because of the importance of the redox reaction, for example, the radical promoting effect of strong nucleophiles (e.g.,  $\text{OCH}_3^-$ ,  $\text{OH}^-$ ) on hydroperoxides in sulfur dioxide observed by Mazzolini et al.<sup>78</sup> may be attributable to inhibition of the acid-catalyzed heterolytic hydroperoxide cleavage.

Because sulfur dioxide takes part in the propagation as well as the initiation reactions, its influence on the rate of initiation is affected by the course of the propagation reaction. Both of the reactions described above tend to cause a rapid decrease in the radical concentration during the course of the polymerization reaction. The hydroperoxide is consumed by the competitive acid-catalyzed reaction and the other component of the redox initiating system, sulfur dioxide, is consumed by polymerization. The initiation mechanism is similar to one involving induced decomposition of an initiator by solvent or monomer discussed by Tobolsky and Matlack<sup>119</sup> as well as the "dead-end" polymerization technique used

by Tobolsky et al.<sup>120</sup> to evaluate both  $k_d$ , the rate constant of initiator decomposition, and the rate constant ratio,  $k_p^2/k_t$ , from one series of experiments.

The following reactions may be involved in the decomposition of the initiator and the formation reactions of free radicals:



where I represents the initiator (t-butyl hydroperoxide in the present study) and H and A represent the di-t-butyl peroxide and sulfuric acid formed by the heterolytic initiator decomposition. The initiation of the polymerization to form the first polymer radical probably occurs via the addition of a sulfite primary radical,  $\dot{S}O_3H$  or  $\dot{S}O_3R$ , to cyclohexene due to polar attraction. The rate of initiation of polymerization is given by the equation:

$$R_i = d[R^\bullet]/dt = k_i[D][R^\bullet] = 2fk_d[S][I] \quad (3-33)$$

where f is the efficiency of utilization of the radicals produced by the decomposition reaction in initiating polymer chains. The difference in reactivity toward monomer of the two primary radicals,  $RO\dot{S}O_2$  and  $HO\dot{S}O_2$ , found by Flockhart, et al.<sup>81</sup> would be expected to result in a relatively low value of f.



The rate of initiator decomposition is related to the concentrations of sulfur dioxide and initiator by the equation:

$$- d[I]/dt = k_d[S][I] + k_h[S][I]^2 \quad (3-34)$$

Because the heterolytic decomposition has been reported to be completed in minutes,<sup>82</sup> the value of the heterolytic decomposition constant,  $k_h$ , must be sufficiently high that the initiator concentration cannot be assumed to be essentially constant during the polymerization as usually found in polymerization reactions initiated by peroxide decomposition products.

The sulfur dioxide concentration decreases by reaction with initiator to produce radicals and by addition of this monomer to the growing polymer chain:

$$- d[S]/dt = k_d[S][I] + k_h[S][I]^2 + k_1[S\cdot][D] - k_{1R}[S\cdot] \quad (3-35)$$

Because the initiator concentration is relatively low, the first two terms in the above equation may be assumed to be negligible compared to the second two and the decrease in sulfur dioxide concentration is approximately equal to the decrease resulting from the propagation reaction alone.

The decrease in cyclohexene concentration may be accounted for by participation of this comonomer in the polymerization initiation reaction (i.e., formation of the first unit of the polymer chain), and by participation in the

propagation reaction:

$$-d[D]/dt = k_1[R\cdot][D] + k_2[S\cdot][D] - k_{2R}[D\cdot] \quad (3-36)$$

For this monomer as well, the first reaction contributes very little toward the total reduction in monomer concentration and may therefore be neglected. Thus, the relationship between the temporal decrease in the logarithm of the charge-transfer complex optical density and the concentration of the reagents derived above is essentially unaffected by the initiation reactions. Substitution of the equation relating  $R_i$  to the concentrations of the components of the initiating system into equations (3-27) to (3-29) leads to the following equations for each of the assumed controlling modes of termination for:

(1) alkyl biradical termination: (3-37)

$$-\frac{d\ln OD}{dt} = \left( \frac{fk_d[S][I]}{k_{tDD}} \right)^{\frac{1}{2}} \left( \frac{1}{[S]} + \frac{1}{[D]} \right) \left( \frac{k_1k_2[S][D] - k_{1R}k_{2R}}{k_{1R} + k_2[D]} \right)$$

(2) cross-termination: (3-38)

$$-\frac{d\ln OD}{dt} = \left( \frac{fk_d[S][I]}{k_{tSD}} \right)^{\frac{1}{2}} \left( \frac{1}{[S]} + \frac{1}{[D]} \right) \left( \frac{k_1k_2[S][D] - k_{1R}k_{2R}}{\sqrt{(k_{1R} + k_2[D])(k_{2R} + k_1[S])}} \right)$$

(3) sulfonyl biradical termination: (3-39)

$$-\frac{d\ln OD}{dt} = \left( \frac{fk_d[S][I]}{k_{tSS}} \right)^{\frac{1}{2}} \left( \frac{1}{[S]} + \frac{1}{[D]} \right) \left( \frac{k_1k_2[S][D] - k_{1R}k_{2R}}{k_{2R} + k_1[S]} \right)$$

Similar equations to those derived above may be obtained to assess the influence of reagent concentrations on the other experimentally determined variable, the sulfur dioxide concentration during the reaction. The ratio of the rate of decrease of the logarithm of the optical density to the logarithm of sulfur dioxide concentration is independent of the initiation reaction. For the polymerization of alternating copolymers this ratio is given by the expression:

$$\frac{d\ln OD/dt}{d\ln[S]/dt} = \frac{d\ln OD}{d\ln[S]} = \frac{[S] + [D]}{[D]} \quad (3-40)$$

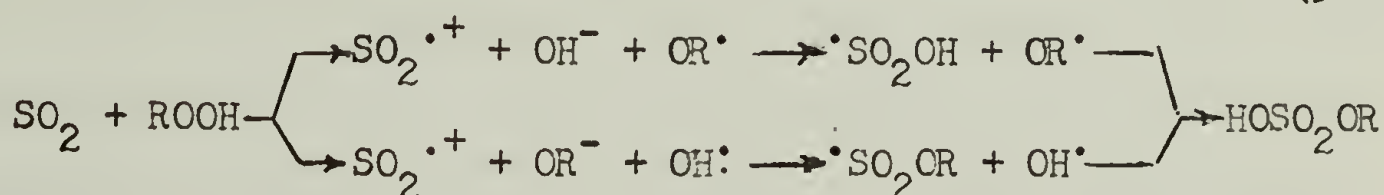
The rate of decrease of the logarithm of the sulfur dioxide concentration expressed as a function of the initiator and comonomer concentration is given by substituting the term  $1/[S]$  for the term  $(1/[S] + 1/[D])$  in equations (3-37) to (3-39).

Primary radical termination. In an alternate reaction pathway for the disappearance of radicals formed in the initiation reaction, the radicals formed by the sulfur dioxide-induced homolytic decomposition of t-butyl hydroperoxide can be postulated to recombine to form inactive products. By this mechanism competition for radicals occurs between the polymerization initiation and primary radical recombination processes. Schulz and Banihaschemi<sup>69</sup> postulate a reaction mechanism of this

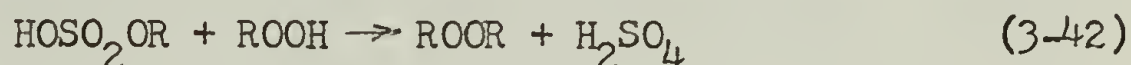


kind for the formation of a cationic initiator for the homopolymerization of styrene in sulfur dioxide, attributing the cationic initiation to the t-butyl half-ester of sulfuric acid. Based on the investigations of Schulz and Banihaschemi,<sup>69</sup> Chien and Boss<sup>82</sup> and Flockhart, et al.,<sup>81</sup> possible reaction mechanisms for the formation of this half-ester are presented below:

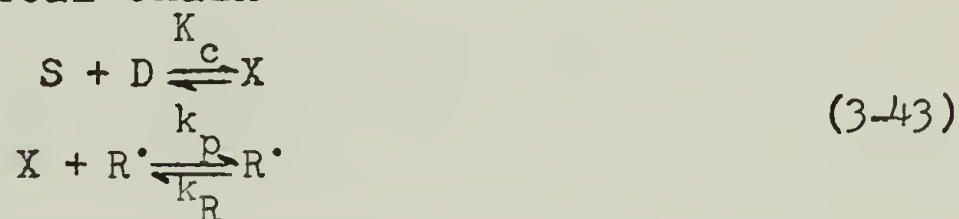
(3-41)



furthermore, reaction (3-42) may occur to form an inactive peroxide:



IIIil(d). Charge-transfer complex homopolymerization, propagation. A mechanism for the formation of alternating copolymers from certain monomer pairs proposed by numerous investigators, is for propagation to occur by the addition of monomer units consisting of an equimolar charge-transfer complex to a radical chain:



where X is the charge-transfer complex, R<sup>·</sup> is the growing radical chain, K<sub>c</sub> is the charge-transfer complex equilibrium constant and k<sub>p</sub> and k<sub>R</sub> are the propagation and de-propagation rate constants. The rate of change of the logarithm of the charge-transfer complex optical density

is given by:

$$-\frac{d\ln OD}{dt} = [R^\bullet] \left( \frac{k_p K_c [S][D] - k_R}{K_c [S][D]} \right) \quad (3-44)$$

Termination. If propagation via the charge-transfer complex is assumed, all of the polymer chains are most likely to have identical terminal radicals and only one termination reaction is believed to be possible. The radical chain end can either be of hydrocarbon  $\sim SD^\bullet$ ; or of sulfonyl,  $\sim DS^\bullet$ ; character; either being formed by the addition of molecules of complex in a direction determined by the polarity of the initiating radical. Since  $ROSO_2^\bullet$  and/or  $HO\dot{S}O_2$  are formed by the initiating system used in this investigation, it is probable that the sulfonyl moiety in the growing chain possesses the free electron. Thus, if propagation occurs via the charge-transfer complex, termination of sulfonyl radicals is likely. The termination reaction, assuming propagation by reaction of the complex only, may be written as:



where  $k_t$  is the termination rate constant. The decrease in the logarithm of the optical density of the complex is given by the following relationship if a steady-state radical concentration is assumed:

$$-\frac{d\ln OD}{dt} = \left( \frac{R_1}{2k_t} \right)^{\frac{1}{2}} \left( \frac{k_p K_c [S][D] - k_R}{K_c [S][D]} \right) \quad (3-46)$$

Initiation. Although participation of some sulfur dioxide-olefin charge-transfer complexes in the initiation reaction has been reported, presumably because of homolysis of unstable complexes by radiant energy, no evidence for the spontaneous initiation of the copolymerization of sulfur dioxide and cyclohexene has been presented. Under the experimental conditions used in this investigation it was shown that an external source of free radicals was required to initiate this copolymerization. It may be assumed, therefore, that the charge-transfer complex is not involved in the initiation reaction. The decrease of the logarithm of the complex optical density with time is unaffected by the presence of the complex and may be expressed as a function of the reagent concentrations by the equation:

$$-\frac{d\ln OD}{dt} = \left( \frac{fk_d [S] [I]}{k_t} \right)^{\frac{1}{2}} \left( \frac{k_p K_c [S] [D] - k_R}{K_c [S] [D]} \right) \quad (3-47)$$

The ratio of the rate of decrease of the logarithm of optical density to that of the sulfur dioxide concentration is given by equation (3-40).

$$\frac{d\ln OD/dt}{d\ln [S]/dt} = \frac{[S] + [D]}{[D]} \quad (3-40)$$

The rate of decrease of the logarithm of the sulfur dioxide concentration for propagation by the charge-transfer



complex is related to the reagent concentration by the expression:

$$-\frac{d\ln[S]}{dt} = \left( \frac{fk_d[S][I]}{k_t} \right)^{\frac{1}{2}} \left( \frac{[D]}{[S] + [D]} \right) \left( \frac{k_p K_c [S][D] - k_R}{K_c [S][D]} \right) \quad (3-48)$$

The depropagation rate constant,  $k_R$ , may be expressed in terms of the propagation rate constant, the charge-transfer complex equilibrium constant and the concentrations of the comonomers at equilibrium,  $[S]_e$  and  $[D]_e$ , in an equation derived by equating the rate of change of complex concentration to zero when equilibrium is attained:

$$k_R = k_p K_c [S]_e [D]_e \quad (3-49)$$

IIIi2. Qualitative discussion of rate data. Data relating the logarithm of the optical density of the charge-transfer complex in methylene chloride to the time of observation are presented in Figures 18, 19, 20 and 21. The logarithm of the sulfur dioxide concentration is related to time in Figures 22 and 23. As expected, the logarithms of both the charge-transfer complex optical density and the sulfur dioxide concentration decrease during the polymerization. The rates of decrease do not remain constant but decrease during the reaction, so that after 60 to 70 minutes both optical density and sulfur dioxide concentration remain constant at a level above that of the complete conversion of the comonomers.

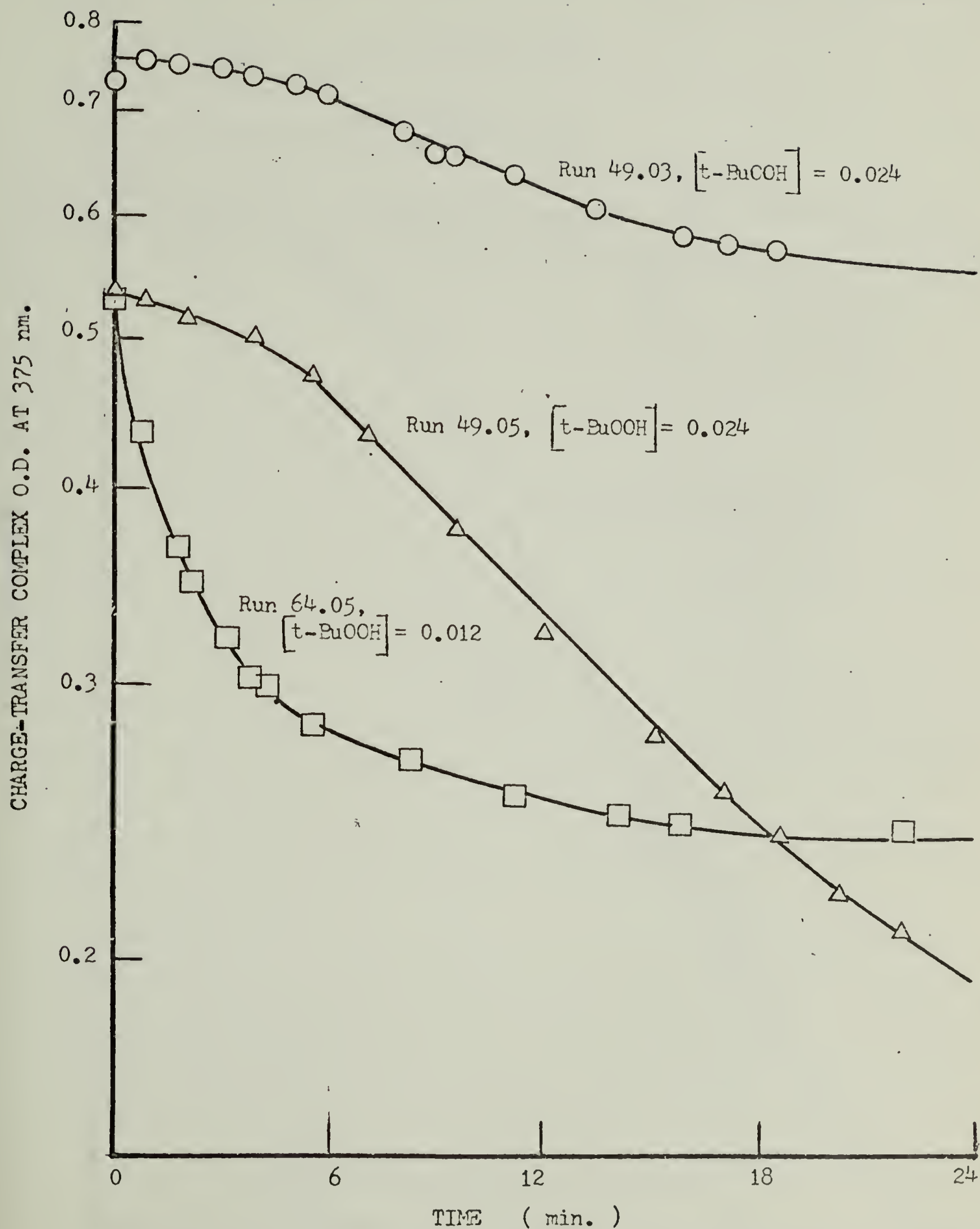


Figure 18. Charge-transfer complex optical density during polymerization in dichloromethane at  $-19^{\circ}\text{C}$

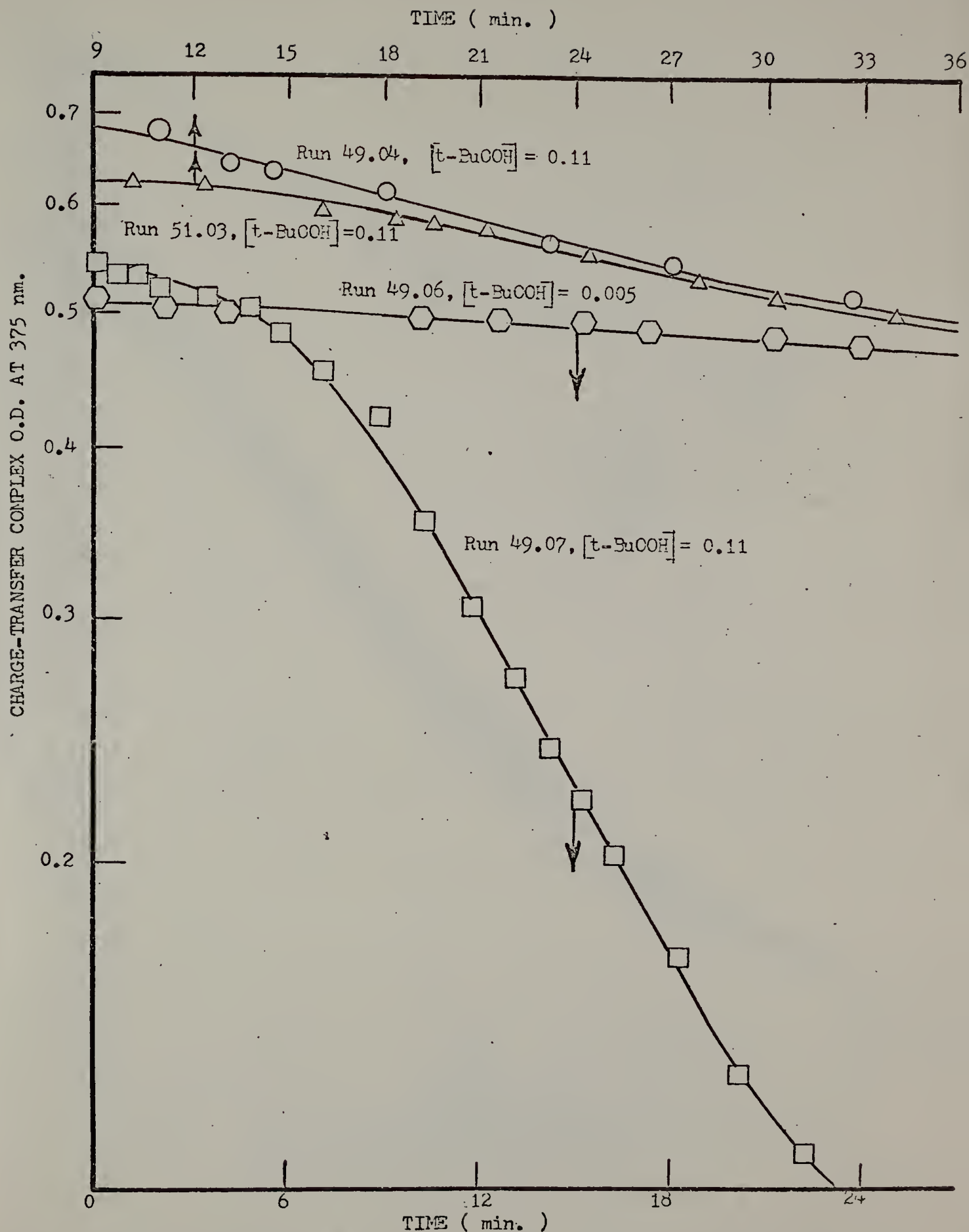


Figure 19. Charge-transfer complex optical density during polymerization in dichloromethane at  $-19^{\circ}\text{C}$



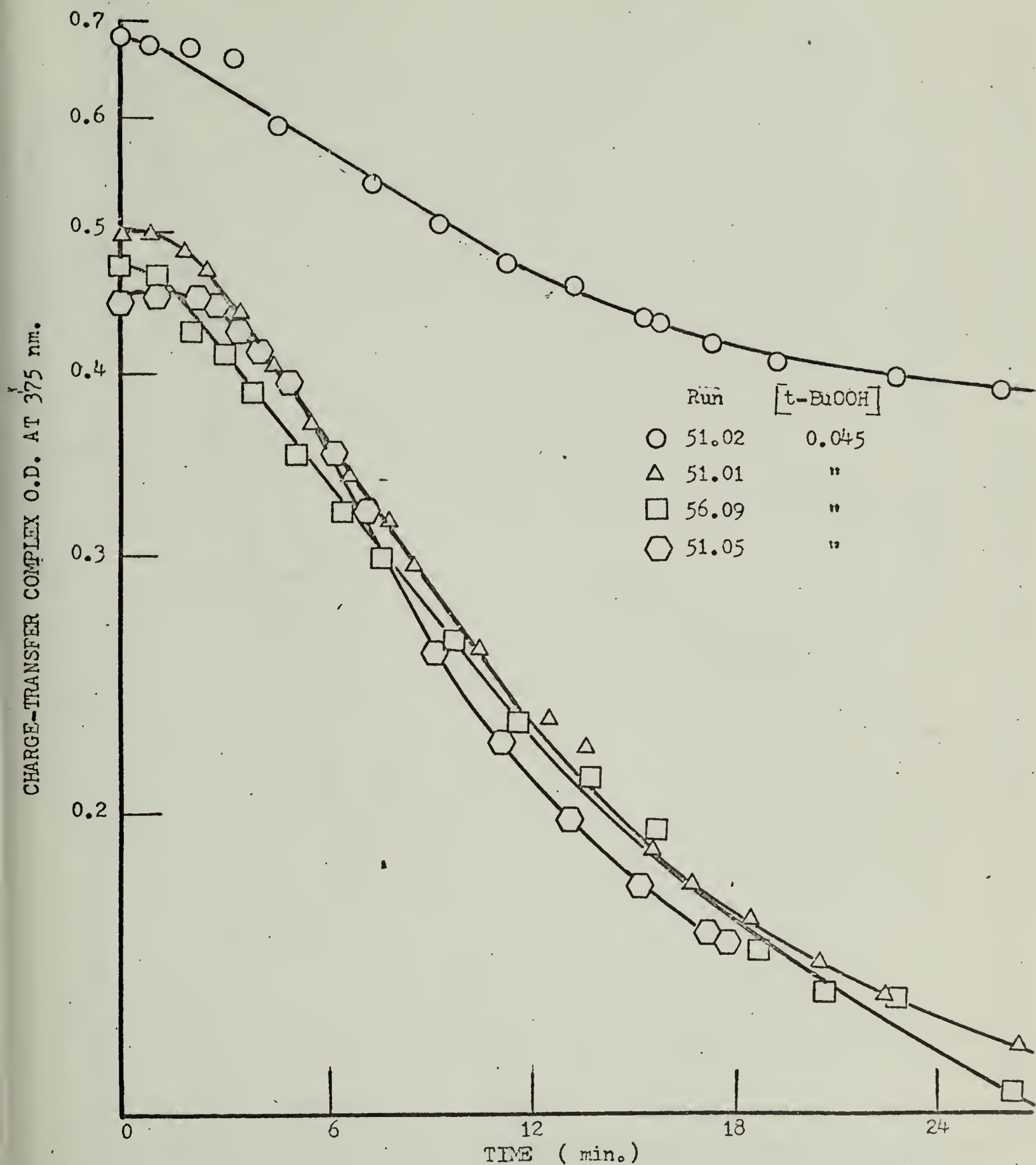


Figure 20. Charge-transfer complex optical density during polymerization in dichloromethane at  $-19^{\circ}\text{C}$

CHARGE-TRANSFER COMPLEX O.D. AT 375 nm.

CHARGE-TRANSFER COMPLEX O.D. AT 375 nm.

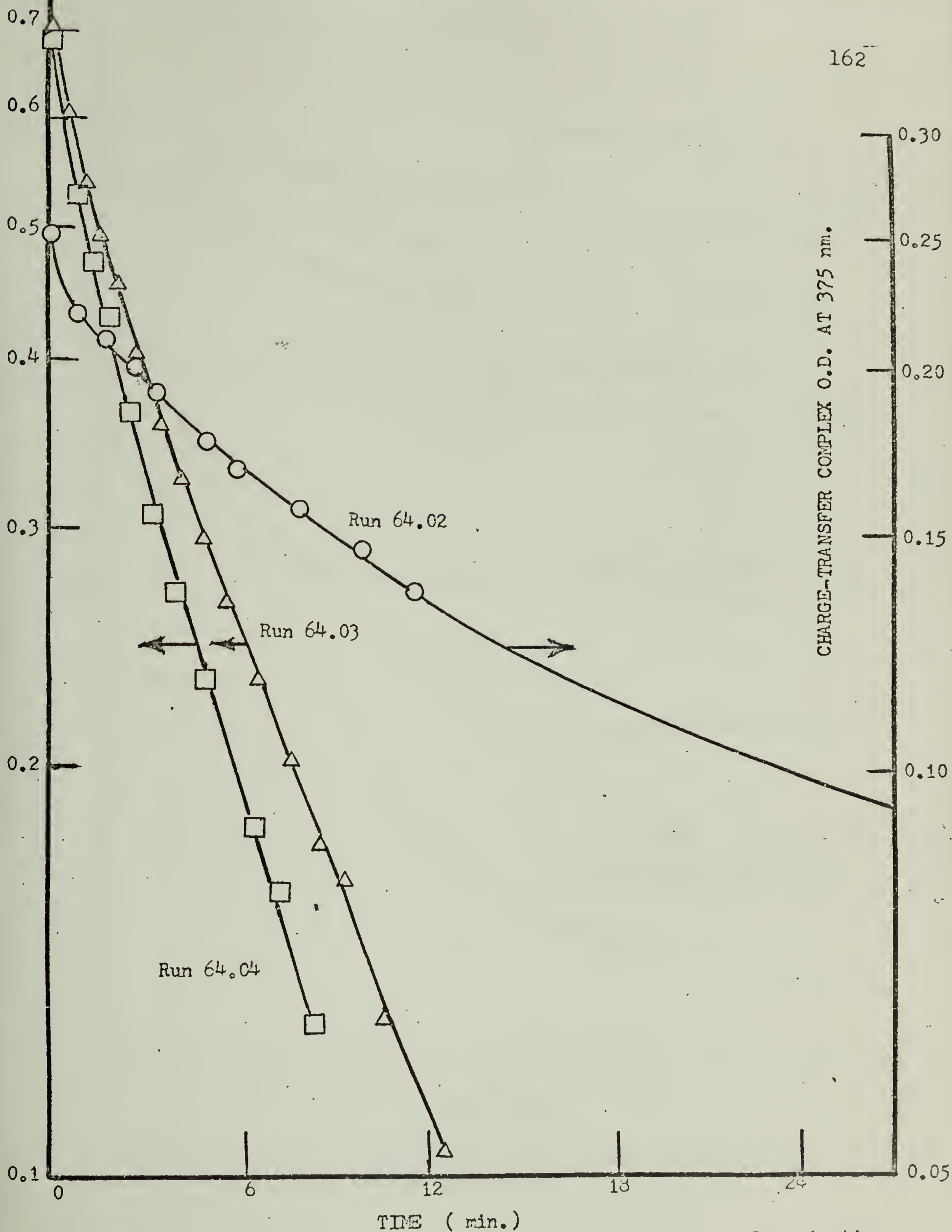


Figure 21. Charge-transfer complex optical density during polymerization in dichloromethane at  $-19^{\circ}\text{C}$ . Initial  $t\text{-BuOOH}$  concentration  $0.045\text{ mol./l.}$

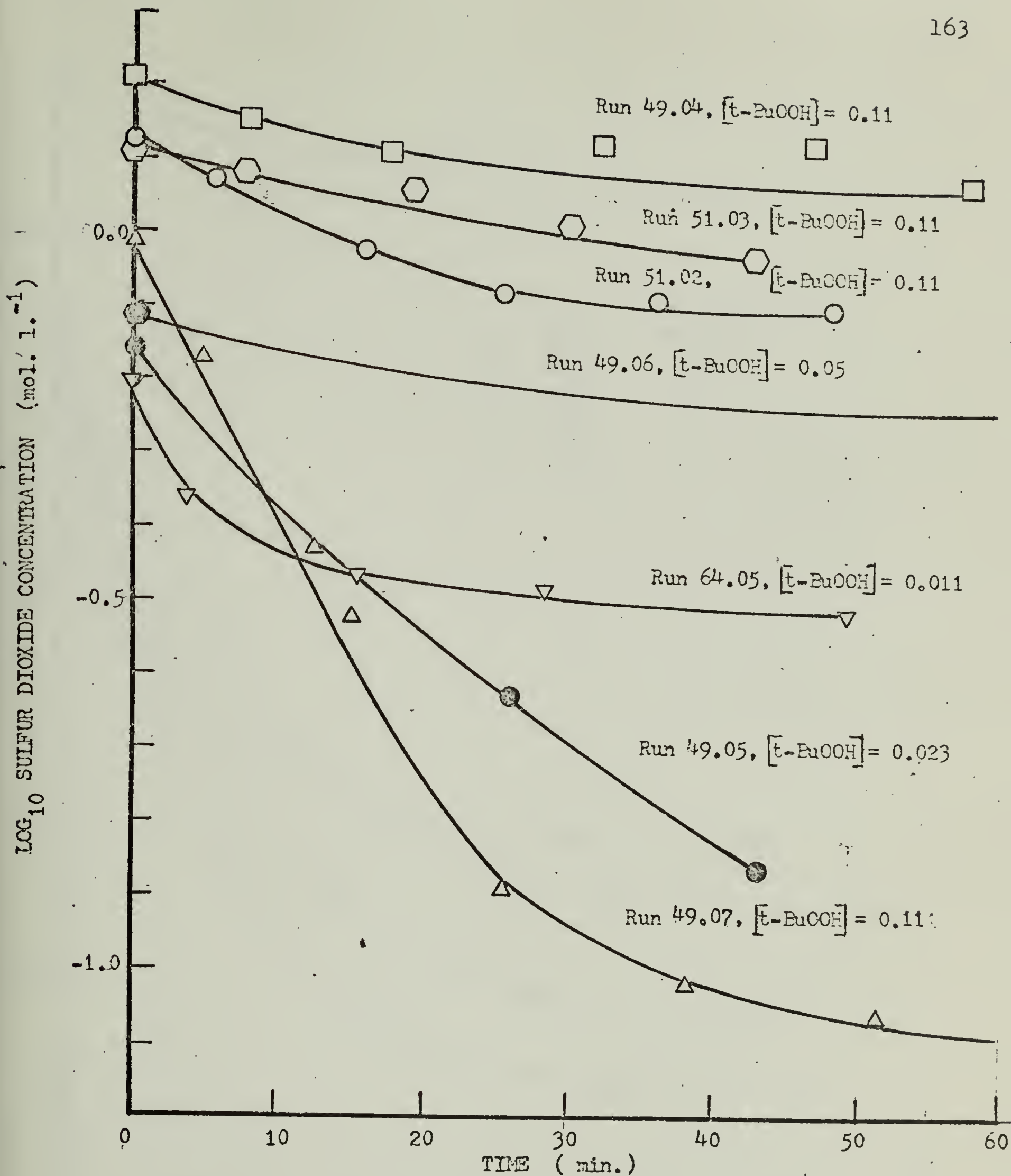


Figure 22. Sulfur dioxide concentration during polymerization in dichloromethane at  $-19^{\circ}\text{C}$



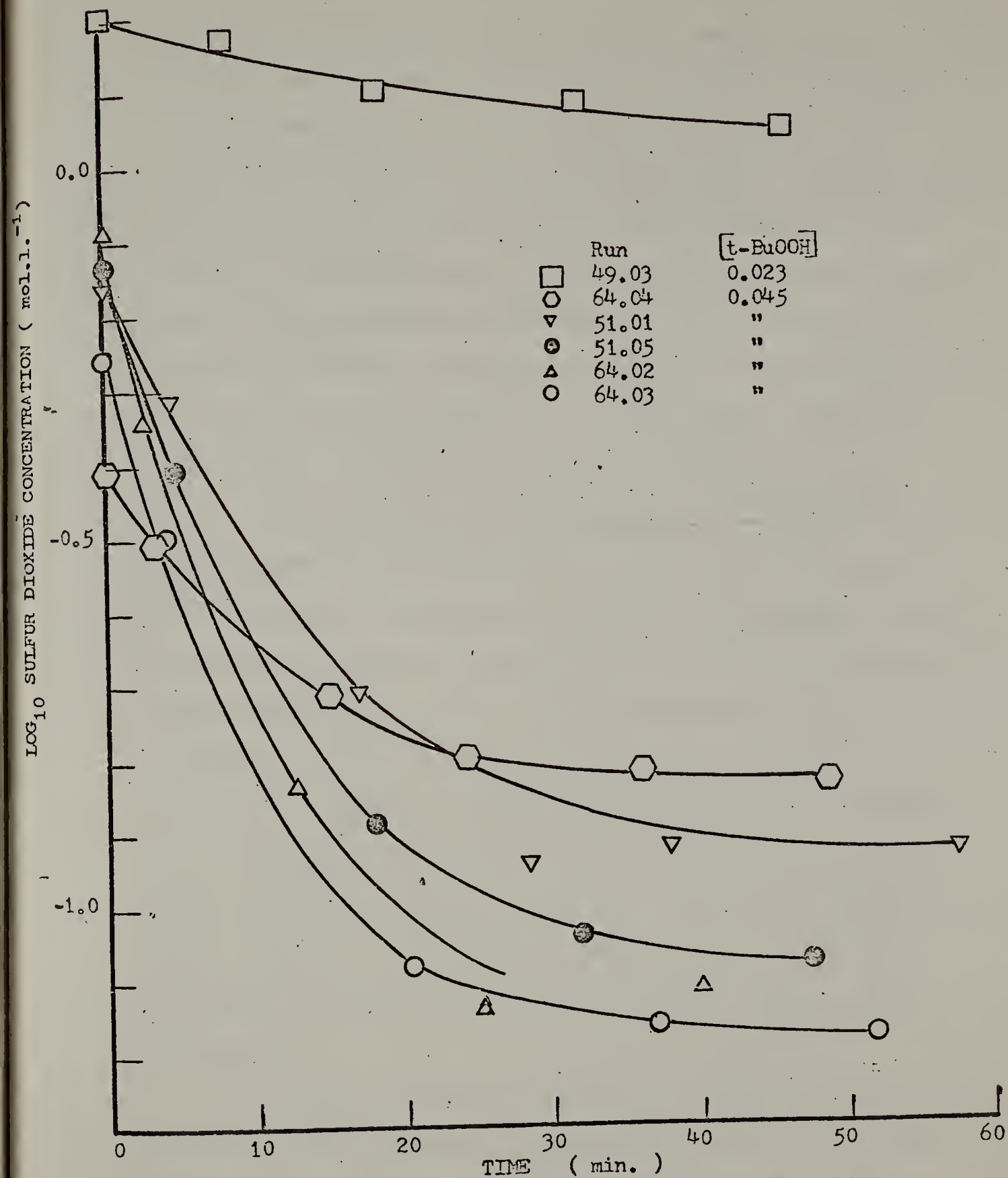


Figure 23. Sulfur dioxide concentration during polymerization in dichloromethane at  $-19^{\circ}\text{C}$

Because the observed equilibrium or limiting monomer concentrations are well above that of complete exhaustion of the comonomers and are influenced strongly by initiator concentration, it appears probable that the major cause of the decrease in the rates of change of logarithmic concentrations is a significant decrease in the free radical concentration during the reaction. The approach toward a steady-state monomer concentration as a result of depropagation may also exert a small contribution to leveling out of the curves.

A demonstration of the influence of initiator on the progress of the reaction is presented in Figure 24. The reaction illustrated was readily reinitiated after reaching an apparent equilibrium or limiting conversion when additional initiator was introduced. If the decrease in slope of the monomer concentration-vs.-time curves is assumed to be influenced mainly by a significant decrease in the free radical concentration during the reaction, an indication of the rate of decrease of the initiator concentration is provided by the rate of decrease of the slopes of the curves,  $-d^2(\text{concentration})/dt^2$ .

In addition to the decrease in slope occurring at the end of the reaction, the optical density data also exhibit anomalous slopes at the beginning of the runs.

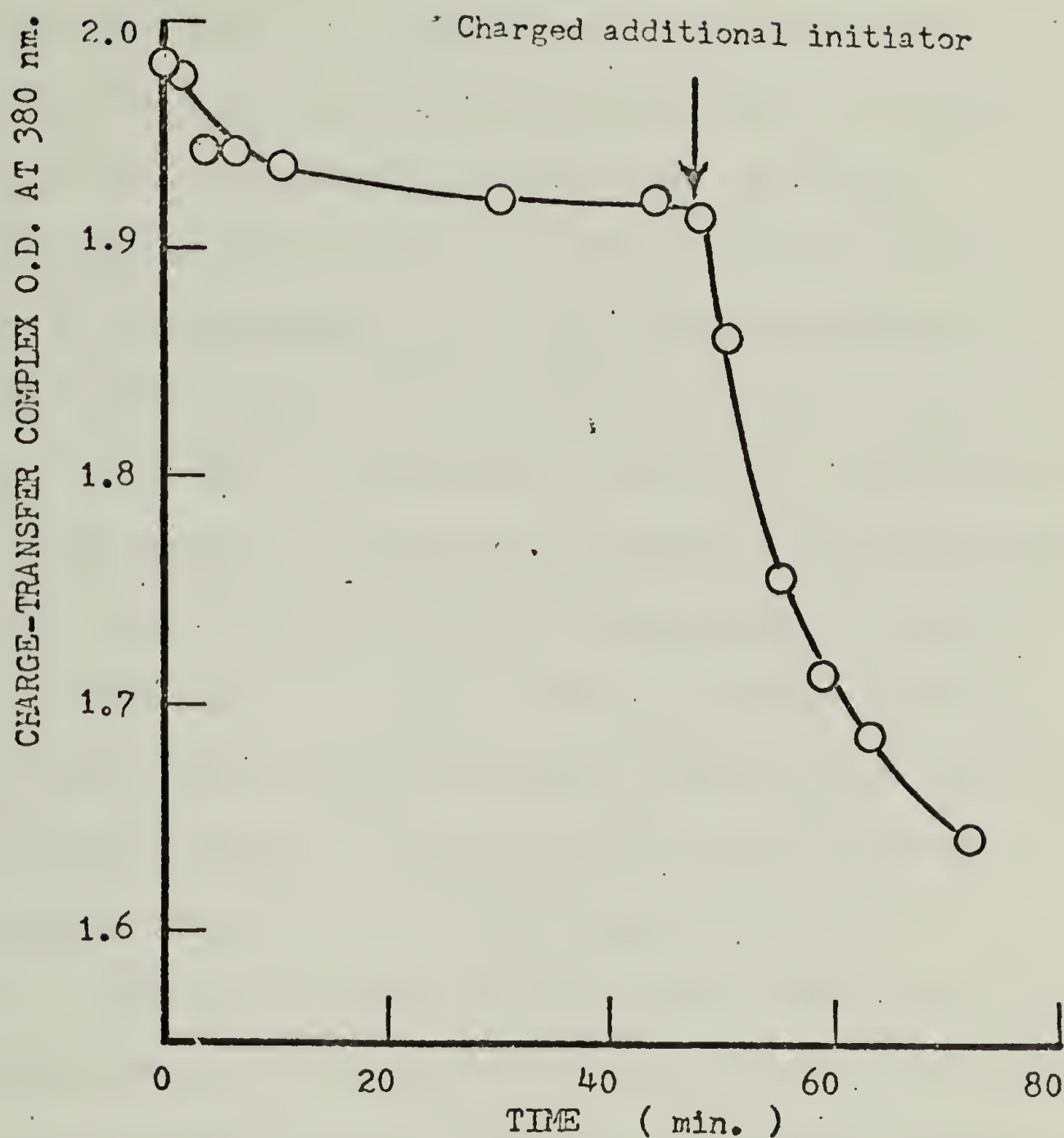


Figure 24. Effect of initiator charge during polymerization  
 Run 19.02;  $[\text{SO}_2]_0 = 0.90 \text{ mol.l.}^{-1}$ ;  
 $[\text{C}_6\text{H}_{10}]_0 = 1.66 \text{ mol.l.}^{-1}$ ; Temp. =  $-18.6^\circ\text{C}$ ;  
 $[\text{t-BuOOH}]_0 = 0.003 \text{ mol.l.}^{-1}$ ;  
 $[\text{t-BuOOH}]_{\text{final}} = 0.078 \text{ mol.l.}^{-1}$



In most of the plots of the logarithm of optical density-vs.-time, the initial rate of change was found to be quite slow or zero. As shown in Table X, the duration of the initial, slow rate period was found to increase roughly as the initiator concentration increased.

This phenomenon was not observed in the sulfur dioxide-vs.-time curves even for those experiments exhibiting fairly long observed optical-density induction periods. It must be concluded, therefore, that the observed phenomenon is an artifact of the measurement as discussed below, rather than a consequence of the reaction kinetics. The lack of correspondence between optical density and sulfur dioxide concentration measurements in this region is attributed to the presence in the reaction mixture of a heteroclytic decomposition product of the initiator. As described more fully in a later section, this initiator decomposition is accompanied by the formation of a second phase which causes a light scattering effect. The contribution to the optical density by light scattering causes the optical density to decrease more slowly than the charge-transfer complex concentration during the initial period. In addition, some contribution to the slow initial rate of decrease of optical density by initial inhomogeneity in initiator concentration (i.e., incomplete mixing) cannot be

TABLE X

Effect of Initiator Concentration on Induction Period

t-Butyl Hydroperoxide Concentration, mol l <sup>-1</sup>	Duration of Induction Period, min.
0.110	19,16,11
0.045	3,2,1,1,0,0
0.023	6,5
0.012	0
0.005	0

completely ruled out. The observation that the induction period increased as the initiator concentration increased makes it improbable that the induction is due to inhibition of the polymerization reaction.

For a significant time between the initial and final variable rate periods, the rates of decrease of the logarithms of both optical density and sulfur dioxide concentration are approximately constant. During this period of approximately constant slope, the initiator concentration is sufficiently high that its decrease with time probably has a negligible effect on the polymerization kinetics. That this is not true at low initiator concentrations is shown by the curves for Run 64.05 (Figures 18 and 22), for which the straight line approximation is obviously invalid. When the logarithm of a measured concentration decreases at a constant rate, the ratio of the concentration functions which describe the rate of decrease of the measured concentration does not vary with time. Thus, measured values of these concentrations at any time, e.g., at initial conditions, will yield the same values of the rate constants. Testing of alternative mechanisms may be performed by substituting experimentally determined rates of logarithmic concentration decrease and initial reactant concentrations into the differential equations derived from the postulated



mechanisms (Equations (3-37) to (3-39) and (3-47) and analogues for sulfur dioxide concentrations).

IIIi3. Copolymer composition. The data presented in Table V demonstrates that equimolar copolymer is formed independent of the starting comonomer composition and polymerization temperature within the limits of experimental error. The average value of the copolymer composition ratio,  $d [D]/d [S]$ , calculated from the elemental analyses for carbon and sulfur equals 1.00 with a standard deviation of 0.06 (95% confidence limits equal to 0.16). This confirms that propagation occurs either by perfectly alternating addition of the comonomers or by addition of an equimolar charge-transfer complex.

IIIi4. Propagation and termination mechanisms at  $-19^{\circ}\text{C}$ . Equations describing the rates of decrease of the logarithms of the optical density ((3-27) to (3-29) and (3-47)) and the sulfur dioxide concentration for assumed propagation mechanisms of reversible alternating comonomer addition and reversible charge-transfer complex addition have been derived above. In these equations the existence of a steady-state concentration of radicals is assumed. Although the rate of initiation was found to vary with time, the assumption of a steady-state concentration of radicals at any one time, i.e., equality of the rates of radical appearance and disappearance,

is valid. A decrease in the rate of initiation, occasioned by a decrease in the initiator concentration, is presumed to be accompanied by an equivalent decrease in the termination rate since the radical formation and disappearance processes are much more rapid than the reduction in initiator concentration.

In these equations the initiation process is assumed to be second order in the two components of the redox system, sulfur dioxide and t-butyl hydroperoxide. When the initiation rate remains substantially constant, as in the constant slope portions of the plots of the logarithms of concentration vs. time, the equations relating rates to concentrations for the two possible modes of chain propagation and the three controlling termination mechanisms possible in one of these models may be written in the following forms:

(1) for alternating propagation with alkyl biradical termination:

$$Y_S = Y_{OD} = C(k_{1R} + k_2[D]) \quad (3-50)$$

(2) for alternating propagation with cross-termination: (3-51)

$$Y_S = Y_{OD} = C \sqrt{k_1 k_2 ([S][D] + [S]_e [D]_e) + k_2 k_{2R} [D] + k_1 k_{1R} [S]}$$

(3) for alternating propagation with sulfonyl biradical termination:

$$Y_S = Y_{OD} = C(k_{2R} + k_1[S]) \quad (3-52)$$

(4) for charge-transfer complex propagation:

$$Y'_S = Y'_{OD} = C' \quad (3-53)$$

where:

$$Y_S = \frac{Z}{d \ln [S] / dt} \quad Y_{OD} = \frac{Z([S] + [D])}{[D] (d \ln OD / dt)}$$

$$Y'_S = \frac{Z}{([S] + [D]) (d \ln [S] / dt)} \quad Y'_{OD} = \frac{Z}{[D] (d \ln OD / dt)}$$

$$C = \left( \frac{k_t}{fk_d} \right)^{\frac{1}{2}} \left( \frac{1}{k_1 k_2} \right) \quad C' = \left( \frac{k_t}{fk_d} \right)^{\frac{1}{2}} \left( \frac{1}{k_p} \right)$$

$$Z = ([S] [I])^{\frac{1}{2}} \left( \frac{[S] [D] - [S]_e [D]_e}{[S]} \right)$$

These equations are identical to those derived in sections IIII1(c) and IIII1(d) with exception of the fact that the expression  $(k_1 k_2 [S] [D] - k_{1R} k_{2R})$  has been replaced by its equivalent in terms of equilibrium monomer concentrations,  $k_1 k_2 ([S] [D] - [S]_e [D]_e)$ . This transformation was made to permit a straight-forward evaluation of the experimental data since values of the equilibrium monomer concentration product,  $[S]_e [D]_e$ , for the copolymerization of sulfur dioxide and cyclohexene may be obtained from the data of Cook, Dainton and Ivin.<sup>93</sup> The equilibrium monomer concentration product calculated from these literature results is presented as a function of temperature in Figure 15. Testing of the alternative mechanisms may be carried out by substituting experimentally determined rates of concentration decrease and initial



reagent concentrations into equations (3-50) to (3-53) and evaluating the fit of the data to the proposed mechanism.

IIII4(a). Effect of comonomer ratio. The rates of decrease of the logarithms of sulfur dioxide concentration and optical density, the initial reagent concentrations and the values of  $Y_S$  and  $Y_{OD}$  calculated from these data are presented in Table XI for eight experiments performed at  $-19^\circ\text{C}$ . A significant increase in the polymerization rate, indicated by both the logarithmic rates of decrease of the sulfur dioxide concentration and the charge-transfer complex optical density, as the ratio of sulfur dioxide to cyclohexene in the initial charge was decreased is evident from these data.

The model derived for propagation by the charge-transfer complex leads to a relationship in which the rate of polymerization is independent of the ratio of the comonomers. This occurs since only one type of radical end group is present. If propagation takes place by the alternating addition of the comonomers, the models derived for this propagation mode predict an increase in the reaction rate as the ratio of sulfur dioxide to cyclohexene decreases, if sulfonyl biradical termination predominates, and a decreasing reaction rate with a decrease in this ratio if the cyclohexyl biradical termination predominates. As shown in equation (3-54), an increase

TABLE XI  
Effect of Comonomer Ratio on Reaction Rate at  $-19^{\circ}\text{C}$

Run	Temp.,	$[I]_0$	$[S]_0$	$[D]_0$	$\frac{[S]_0}{[D]_0}$	$R_{OD}$	$R_S$	Initial Equil.	$Y_{OD}$	$Y_S$	$Y'_{OD}$	$Y'_S$	
Ident.	$^{\circ}C$							$[S][D]$	$[S][D]$				
49.03	-18.5 $\pm$ .7	0.023	1.513	1.510	1.00	0.925	0.675	2.284	0.19	1269	869	420	287
49.05	-18.8 $\pm$ .3	0.023	0.701	3.432	0.20	2.31	2.30	2.405	0.18	494	412	419	100
64.04	-19.7 $\pm$ .4	0.046	0.380	1.887	0.20	1.94	2.85	0.717	0.15	318	180	140	79
56.09	-19.5 $\pm$ .5	0.045	0.655	3.173	0.21	2.93	-	2.077	0.16	538	-	140	-
51.01	-18.8 $\pm$ .4	0.045	0.670	3.355	0.20	2.40	3.60	2.247	0.18	701	390	174	97
51.02	-19.0 $\pm$ .4	0.045	1.281	1.810	0.71	1.38	1.00	3.319	0.18	1293	1045	418	338
51.05	-18.8 $\pm$ .4	0.045	0.539	4.240	0.13	4.31	4.65	2.285	0.18	412	339	86	71
49.07	-19.0 $\pm$ .4	0.116	0.703	3.450	0.20	4.03	3.85	2.427	0.18	710	618	171	149

Remarks:

All concentrations in moles/liter

$R_{\text{OD}} = -100 \times \frac{d \log \text{OD}}{dt}, \text{ min}^{-1}$ ;  $R_{\text{S}} = -100 \times \frac{d \log [\text{S}]}{dt}, \text{ min}^{-1}$

$Y$  in mole  $\times$  sec / liter defined in section III i 4

Equilibrium  $[\text{S}][\text{D}]$  calculated from Reference 93

Temperature range refers to time average standard deviation

in the rate of polymerization with decreasing ratio of sulfur dioxide to cyclohexene indicates that the sulfonyl radical concentration predominates, while a decrease in the polymerization rate with a decrease in this comonomer ratio indicates a predominance of the alkyl radicals.

$$-\frac{d[S]}{dt} = [S\cdot] \left( \frac{k_1 k_2 [S] [D] - k_{1R} k_{2R}}{k_{2R} + k_1 [S]} \right) = [D\cdot] \left( \frac{k_1 k_2 [S] [D] - k_{1R} k_{2R}}{k_{1R} + k_2 [D]} \right) \quad (3-54)$$

Since the magnitude of the reaction rate constants for the slow bimolecular collision reaction depends only slightly on the chemical structure of the colliding radicals;<sup>121</sup> if one of the radical species is in excess, its concentration may be assumed to control the termination reaction (see equation (3-25)). This assumption permits the substitution of equations (3-27) to (3-29) for equation (3-25).

The significant influence of the ratio of comonomers on the rate of polymerization thus indicates that propagation does not occur by addition of a pre-formed charge-transfer complex as monomer. Additionally, the increase in the reaction rate occasioned by an increase in the ratio of cyclohexene to sulfur dioxide is indicative of the predominance of sulfonyl radicals in the reaction. These considerations may be quantified further by examining the influence of monomer concentrations on the values of  $Y$  calculated from the polymerization rate data. If charge-transfer complex propagation is assumed, the



values of  $Y'_{OD}$  and  $Y'_S$  should be independent of the concentration of either of comonomers. The average value of  $1/Y' = k_p (fk_d/k_t)^{1/2}$  (values of  $Y'_{OD}$  and  $Y'_S$  were pooled since no significant difference exists between them) was found to equal  $0.0054 \text{ l mol}^{-1}\text{sec}^{-1}$  and the standard deviation equal to 69% of the average value. The large deviation of the data from an assumed concentration-independent average describes the rather poor fit to a charge-transfer complex propagation model.

Values of  $Y_{OD}$  and  $Y_S$  are plotted against the initial cyclohexene concentration in Figure 25A and against the sulfur dioxide concentration in Figure 25B. According to the equations derived above, a straight line of positive slope should be obtained when  $Y$  is plotted against the cyclohexene concentration if alkyl biradical termination predominates and a linear plot of positive slope should result from the plot of  $Y$  against the sulfur dioxide concentration if sulfonyl biradical termination is the controlling reaction. Figure 25 demonstrates that the alkyl radical termination model does not fit the data while the sulfonyl radical termination model provides a fair fit.

The data plotted in Figure 25B also show that the intercept, equal to  $\frac{k_{1R}}{k_1 k_2} \left( \frac{k_{tSS}}{fk_d} \right)^{1/2}$ , is approximately equal to zero. From this fact it can be inferred that depropagation at  $-19^\circ\text{C}$  is not significant. The value of the

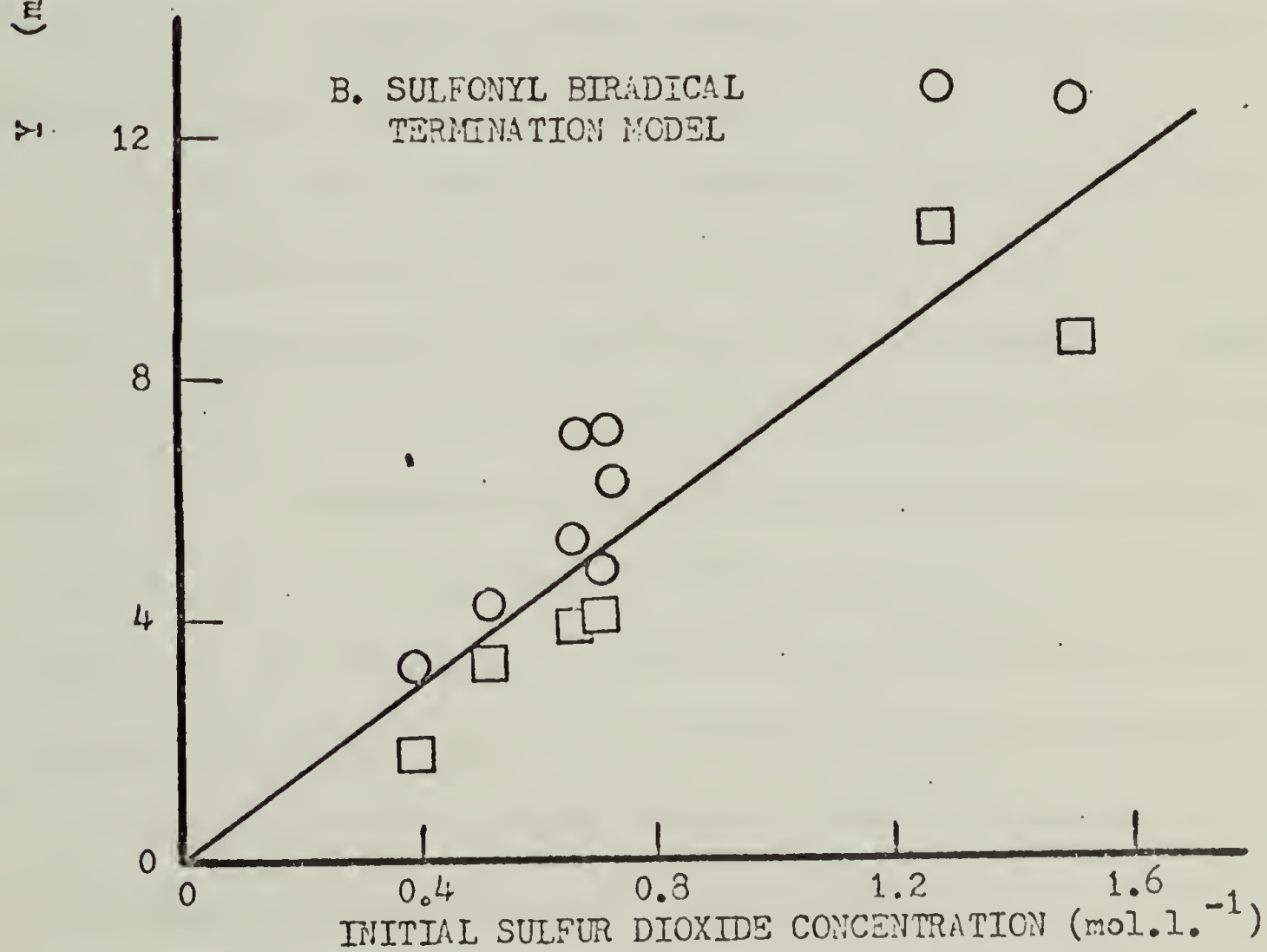
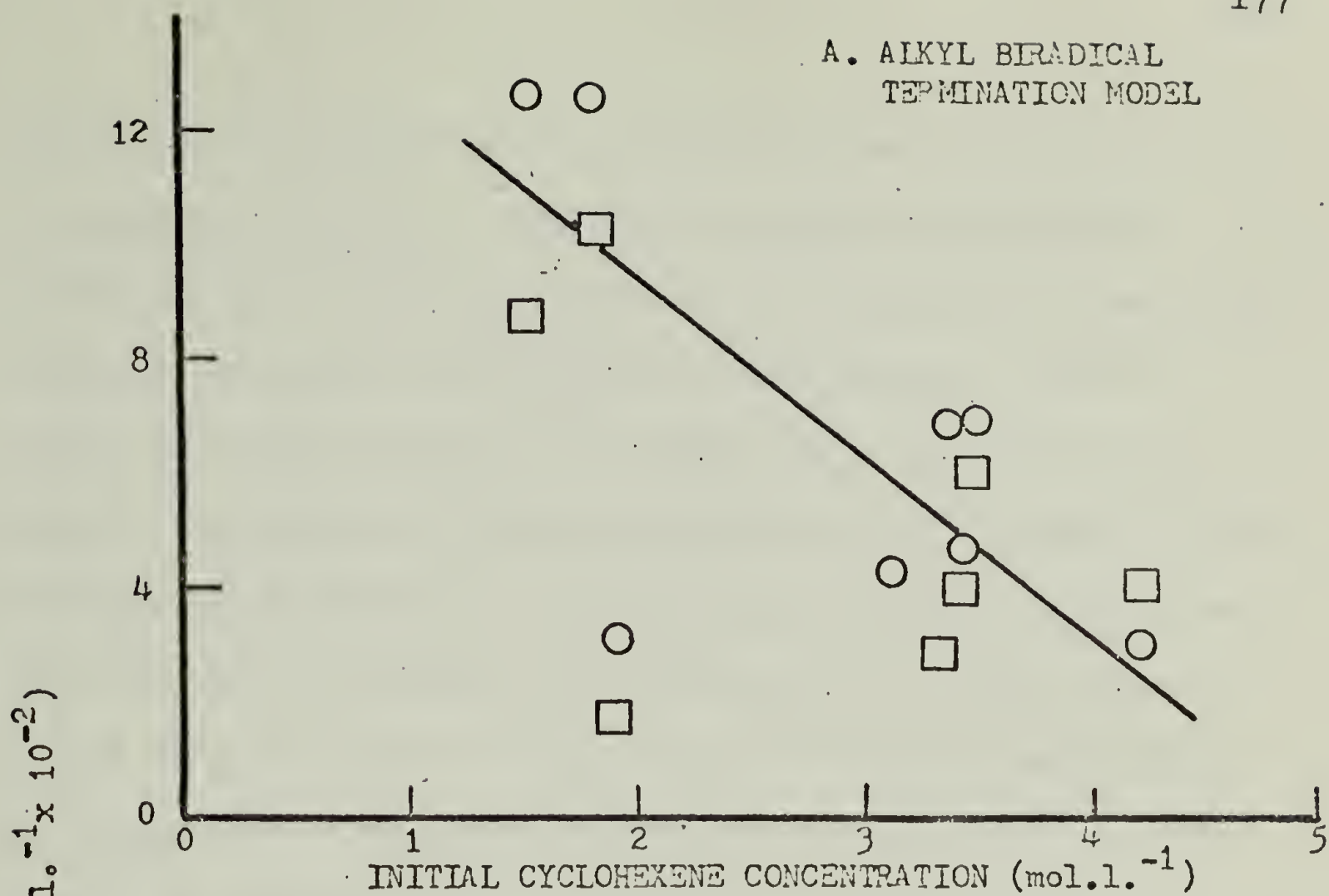


Figure 25. Evaluation of alternating propagation kinetic models

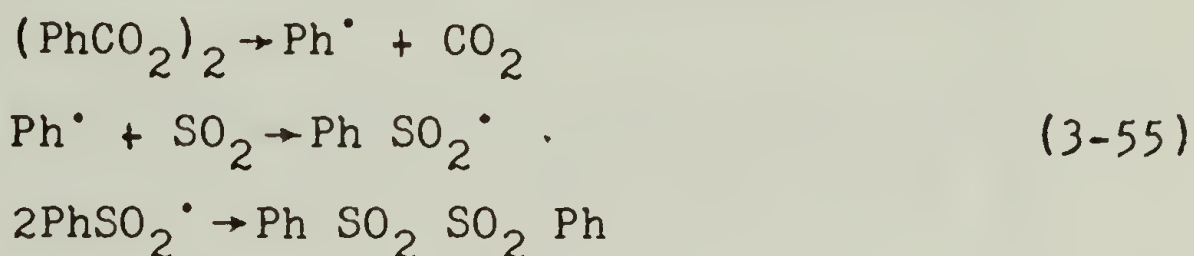
○ Optical density rate data  
 □ SO<sub>2</sub> concentration rate data

ratio of depropagation to propagation rate constants,  $k_{1R}k_{2R}/k_1k_2 = [S]_e[D]_e$ , for the average experimental conditions of the experiments listed in Table XI was calculated to equal 0.08 from the thermodynamic data of Cook, Dainton and Ivin.<sup>93</sup> This tends to confirm the slight importance of depropagation at -19°C shown by the present investigation. The average value of the collection of rate constants,  $k_2(fk_d/k_{tSS})^{1/2}$ , at -19°C calculated from the data of Figure 25B (assuming negligible depropagation) equals  $0.0013 \pm 0.0002 \text{ l mol}^{-1}\text{sec}^{-1}$ . The ratio of standard deviation to average value of the constant describing the alternating addition propagation model, 18%, is significantly better than that of the charge-transfer complex propagation model.

Because the number of data points was too limited to permit correlation, fitting of the data to the three constant crosstermination model was not performed. Predominant termination by the collision of unlike radicals can, thus, not be ruled out. If this is the major mode of termination, the increase in the polymerization rate occasioned by an increase in the initial cyclohexene concentration dictates that  $k_1k_{1R}$  be much larger than  $k_2k_{2R}$ , i.e., that the rate of addition of sulfur dioxide to the cyclohexyl radical be much more rapid than the rate of addition of cyclohexene to the sulfonyl radical.



Although Barb reasoned that sulfonyl biradical termination would be unlikely due to steric hindrance and electrostatic dipolar repulsion,<sup>1</sup> at least one reference to this reaction is found in the literature. Squires and Waters demonstrated the formation of diphenyl disulfone,  $\text{Ph-SO}_2\text{-SO}_2\text{-Ph}$ , from the reaction of benzoyl peroxide and sulfur dioxide,<sup>101</sup> ascribing the formation of this product to the following reaction steps:



Values of  $k_2(fk_d/k_{tSS})^{\frac{1}{2}}$  obtained from the rates of decrease of the logarithms of monomer concentrations in the constant slope period and the initial reagent concentrations are listed in Table XII. These values of the reaction rate constant are based on the assumption of propagation by alternating addition, sulfonyl biradical termination, negligible depropagation and initiation being second order in sulfur dioxide and t-butyl hydroperoxide. This tabulation for the experimentation conducted at  $-19^\circ\text{C}$  includes the experiments listed in Table XI as well as experiments conducted at significantly higher initial total comonomer concentration and at higher and lower initial t-butyl hydroperoxide concentrations. Values of the constant are plotted against the sum of the

TABLE XII

Rate Constants and Second Derivative of Logarithm of Optical Density with respect to Time for Experiments performed at  $-19^{\circ}\text{C}$

Run Ident.	$[\text{I}]_0$	$[\text{S}]_0$	$[\text{S}]_0 + [\text{D}]_0$	$Y_{\text{OD}}$	$Y_{\text{S}}$	$10^4 k_2(\text{fk}_d/k_{\text{tSS}})^{\frac{1}{2}}$	OD Data	$\text{SO}_2$ Data	$-\frac{d^2 \log \text{OD}}{dt^2}$
49.06	0.0046	0.6765	4.06	4197	989	1.611	6.84	-	-
64.05	0.0117	0.6650	4.04	1441	216	4.61	30.79	0.1278	0.1278
49.03	0.0231	1.5131	3.02	1269	869	11.9	17.4	0.0294	0.0294
49.05	0.0234	0.7008	4.13	494	412	14.2	17.0	0.0235	0.0235
64.04	0.0450	0.3803	2.27	318	180	11.9	21.1	0.034	0.034
56.09	0.0448	0.6546	3.82	538	-	12.1	-	0.0354	0.0354
51.01	0.0452	0.6698	4.02	701	390	9.55	17.2	0.0282	0.0282
64.03	0.0444	0.8014	4.80	372	209	21.0	38.3	0.0309	0.0309
64.02	0.0446	0.8531	5.08	320	209	26.6	40.8	0.0275	0.0275
51.02	0.0450	1.2809	3.09	1293	1045	9.9	12.2	0.0302	0.0302
51.05	0.0445	0.5393	4.77	412	339	13.1	15.9	0.032	0.032
49.04	0.114	1.4970	2.99	4287	1934	3.1	7.7	0.035	0.035
51.03	0.113	1.2574	3.04	5562	3570	2.3	3.5	0.035	0.035
49.07	0.116	0.7026	4.16	710	618	9.9	11.4	0.037	0.037

Remarks:

All concentrations in moles/liter

Y in  $\text{mol sec l}^{-1}$  defined in section III i 4 $k_2(\text{fk}_d/k_{\text{tSS}})^{\frac{1}{2}}$  in  $\text{l mol}^{-1}\text{sec}^{-1}$  $-\frac{d^2 \log \text{OD}}{dt^2}$  in  $\text{min}^{-2}$

initial comonomer concentrations,  $[S]_0 + [D]_0$ , in Figure 37. The data shown in Table XII and Figure 37 indicate that, although reasonable constancy is obtained at initial total comonomer concentration less than approximately  $4.7 \text{ mol l}^{-1}$  and intermediate initiator concentrations, appreciable variation in the calculated constant occurs under two conditions. Firstly, the calculated constant increases significantly at high total comonomer concentration. Secondly, a low value of the constant is obtained both at low initiator concentrations, and at a high initiator concentration in the presence of a high sulfur dioxide concentration.

#### IIIi4(b). Effect of total monomer concentration.

Since the equations derived above account for the increase in polymerization rate due to both the increase in propagation rate and the decrease in depropagation rate attending increasing total comonomer concentration, a consistent deviation from these equations must be caused by a phenomenon not associated with the propagation mechanism.

An increase in the rate of polymerization not involving the propagation reaction might arise through an increase in the rate of initiation occasioned by a decrease in recombination of primary radicals at higher monomer concentrations. Recombination of primary radicals is possible since initiation by the t-butyl hydroperoxide



sulfur dioxide system has been shown to produce two radicals of different stabilities.<sup>80</sup>

An alternate possibility is that the rate of termination is decreased at high total monomer concentration due to diffusion control of the termination reaction. Increasing viscosity of the polymerization medium decreases the rate of collision of long polymer chains (i.e., termination) more than the rate of addition of small monomer units to the chain (i.e., propagation) and thus increases the rate of polymerization. This effect may logically be expected to increase as the total monomer concentration increases, because the viscosity of the medium increases very rapidly with increasing polymer concentration in concentrated solutions. A fifth power dependence of viscosity on concentration has been reported.<sup>122</sup> Since the final polymer solution was of syrupy consistency (estimated viscosity 1,000 - 10,000 cp.), diffusion control of termination may be expected. A choice between these possible ways which could lead to an anomalous increase in reaction rate at increased total monomer concentration could not be based on the available data.

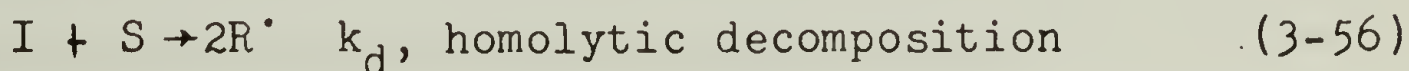
IIIi4(c). Effect of initiator concentration. Significantly lower values of the constant  $k_2(fk_d/k_{tSS})^{\frac{1}{2}}$  were calculated from data obtained from experiments

conducted at low initiator concentrations (Runs 49.06 and 64.05) and at high initiator concentrations and high sulfur dioxide concentrations (Runs 49.04 and 51.03). This can be ascribed to the inability to interpret the temporal behavior of the logarithms of optical density or sulfur dioxide concentration rather than to incorrect choice of reaction mechanism. At high initiator and high sulfur dioxide concentrations, heterolytic decomposition of t-butyl hydroperoxide proceeds very rapidly. This reaction quickly reduces the initiator concentration to a level where the decrease in initiator concentration with time must be taken into account, i.e., where the rate of decrease of the logarithm of monomer concentration decreases continuously. Similar considerations apply to reactions conducted at low initiator concentrations, where a slight absolute decrease in the initiator concentration leads to a large percentage decrease. The effect of low initiator concentration on the kinetic behavior is illustrated by comparing the logarithm of optical density-vs.-time curves for the low initiator concentration experiment, 64.05, to experiments conducted at higher t-butyl hydroperoxide concentrations (Figure 18) and noting that no period of constant slope can be found.

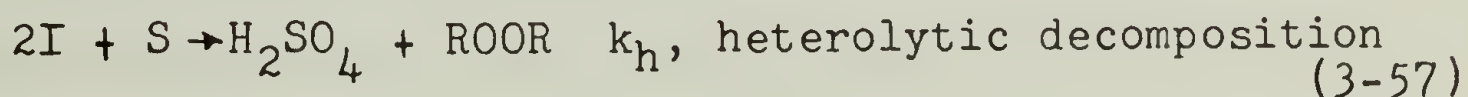
IIIi5. Homolytic decomposition of initiator. The rate of decrease of the logarithms of the charge-transfer

complex optical density and the sulfur dioxide concentration was observed to decrease during the polymerization (Figures 18-23). This decrease in the rate of monomer loss occurs because of a significant decrease in the concentration of one of the reagents, the comonomers and/or the initiator. The ability to reinitiate the polymerization reaction by the addition of initiator after the reaction had reached an apparent equilibrium or limiting conversion is experimental proof that the major cause of the decrease in  $-d[M]/[M]$  is a significant decrease in initiator concentration.

Initiator is consumed both in the formation of radicals:



and in a side reaction which most probably involves the reaction of two moles of t-butyl hydroperoxide to form sulfuric acid and di-t-butyl hydroperoxide: <sup>54</sup>



Because the sulfur dioxide concentration in these experiments was normally much greater than the t-butyl hydroperoxide concentration, the variation in sulfur dioxide concentration represents a smaller relative variation than the variation in the t-butyl hydroperoxide concentration and, thus, may be considered to be essentially constant.



The variation of the t-butyl hydroperoxide concentration with time may then be approximated by the equation:

$$[I] = \frac{1}{(1/[I]_0 + k_h/k_d)(\exp k_d[\bar{S}]t) - 1} \quad (3-58)$$

where  $[\bar{S}]$  equals the average sulfur dioxide concentration.

For the concentrations and times of interest, the exponential term and its coefficient are appreciably greater than one, so that the above equation is closely approximated by:

$$[I] = \frac{\exp - k_d[\bar{S}]t}{1/[I]_0 + k_h/k_d} \quad (3-59)$$

Because the concentration of t-butyl hydroperoxide decreases significantly in relation to the concentrations of the comonomers, the equation relating the rate of decrease of optical density to reagent concentrations may be approximated by an expression containing only the initial initiator concentration and constants. The equation for propagation by alternating addition and sulfonyl biradical termination control under these conditions is:

$$\frac{d \ln OD}{dt} = \left( \frac{fk_d[\bar{S}]}{k_{tSS}(1/[I]_0 + k_h/k_d)} \right)^{\frac{1}{2}} \left( \frac{1}{[\bar{S}]} + \frac{1}{[\bar{L}]} \right) k_1 k_2 \left[ \frac{[\bar{S}][\bar{D}] - [S]_e[D]_e}{k_{2R} + k_1[\bar{S}]} \right] \exp \frac{k_d[\bar{S}]t}{2} \quad (3-60)$$

where all of the pre-exponential terms are essentially constant and  $[\bar{S}]$  and  $[\bar{D}]$  represent the average concentration of sulfur dioxide and cyclohexene, respectively, during the reaction. From this equation, the pseudo-first order decomposition rate constant should equal twice

the negative slope of the logarithm of the rate of decrease of the logarithm of the charge-transfer complex optical density as a function of time.

Plots of this type are presented in Figure 26 for the optical density data. Correlation of the sulfur dioxide concentration data in this manner was not attempted because of the limited number of data points obtained in each experiment and the added uncertainty introduced in obtaining slopes of these curves. Values of the ordinates of Figure 26 were obtained from the slopes of Figures 18-21 (and extensions where required). All of the plots of Figure 26 are reasonably linear and, with one exception, are of approximately equal slope. Values of the slopes are given as  $(d^2 \ln OD / dt^2)$  in Table XII. The mean value and standard deviation of the pseudo-first order decomposition rate constant,  $k_d [\bar{S}]$ , (excluding the one anomalous value) was found to equal  $0.91 \pm 0.18 \times 10^{-4} \text{ sec}^{-1}$  at  $-19^\circ\text{C}$ . This value is within the generally observed order of magnitude of decomposition rate constants for the initiation of free radical polymerization reactions. 120

The pseudo-first order decomposition rate constant of Run 64.05 was found to exceed the values found in the other experiments by a factor of four. The initial t-butyl hydroperoxide concentration of this experiment

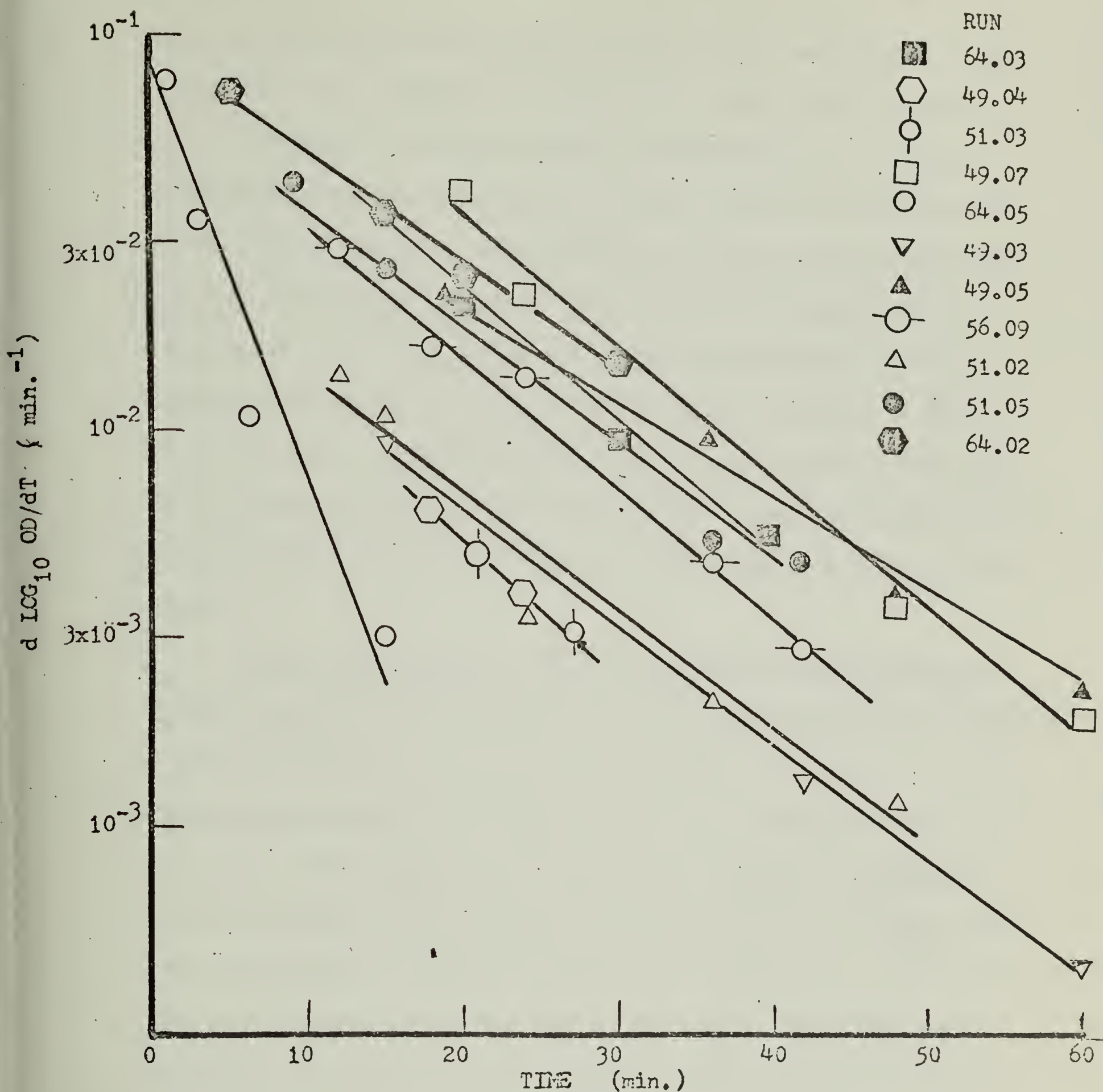


Figure 26. Variation of the rate of change of the charge-transfer complex optical density during polymerization at  $-19^{\circ}\text{C}$



was significantly lower than that of the remainder of the experiments. Failure to obtain the same value of the rate constant is most probably attributable to the assumption made in deriving the model that the relative decrease in comonomer concentration is much less than that of the initiator, and that the comonomer concentration can, thus, be considered relatively constant. The decomposition rate constant of Run 49.06, made at a very low initiator concentration, was not evaluated since the very small decrease in optical density during this experiment precluded determination of the change in slope with time.

#### IIIi6. Temperature effect in propagation reaction.

Data relating the logarithm of the charge-transfer complex optical density to time for experiments conducted at temperatures between  $-1.6$  and  $-48.4^{\circ}\text{C}$  are presented in Figure 27. The logarithm of the sulfur dioxide concentration existing during these runs is plotted in Figure 28. The experiments represented by these figures, as well as those of Runs 51.01 and 56.09 conducted at  $-19^{\circ}\text{C}$ , were made at the same initial reagent concentrations of 0.66 molar sulfur dioxide, 3.3 molar cyclohexene and 0.045 molar *t*-butyl hydroperoxide. These curves exhibit the same general shapes as those of Figures 18-23, an initial slow rate period, a period of constant slope, followed by a falling rate period.

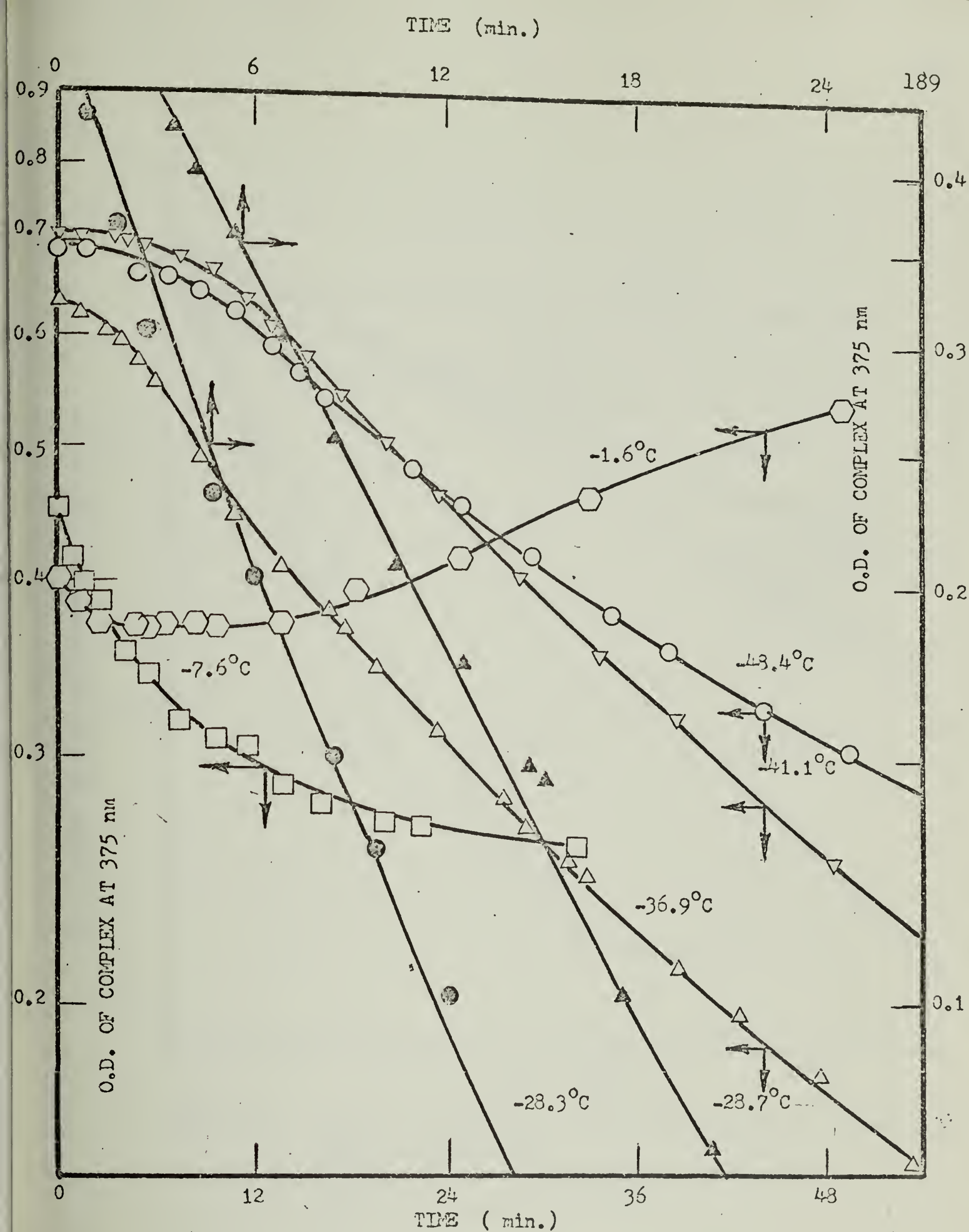


Figure 27. Effect of temperature on the charge-transfer complex optical density during polymerization  
 $[SO_2]_0 = 0.66 \text{ mol./l.}$   $[C_6H_{10}]_0 = 3.3 \text{ mol./l.}$   
 $[t\text{-BuCOH}]_0 = 0.045 \text{ mol./l.}$

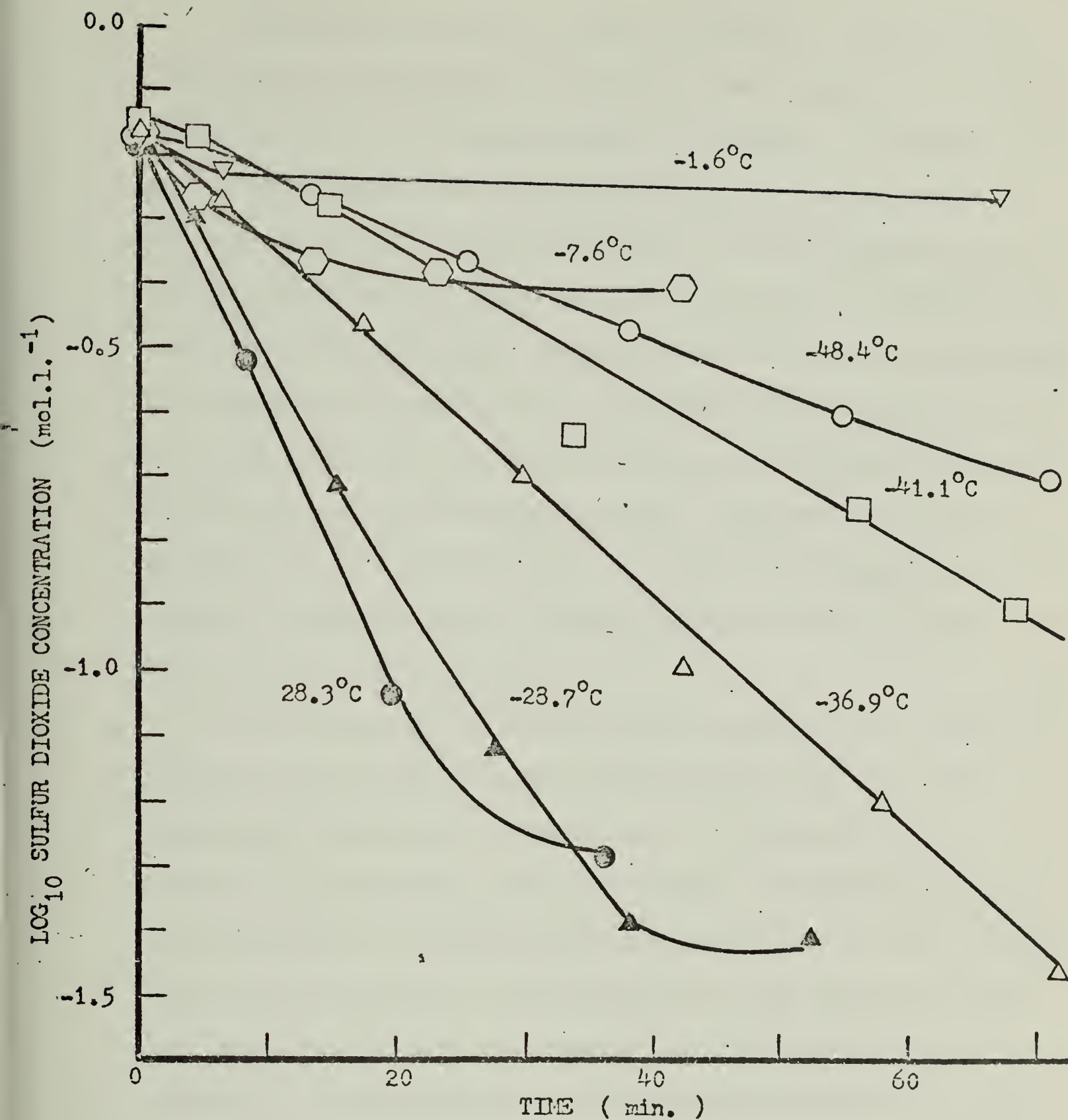


Figure 28. Effect of temperature on the sulfur dioxide concentration during polymerization  
 $[\text{SO}_2]_0 = 0.66 \text{ mol./l.}$   $[\text{C}_6\text{H}_{10}]_0 = 3.3 \text{ mol./l.}$   
 $[\text{t-BuOOH}]_0 = 0.045 \text{ mol./l.}$



The optical density in the experiment conducted at the highest temperature, Run 61.02, was observed to increase with time after an initial decrease. A corresponding increase in the sulfur dioxide concentration was not observed. Rapid darkening of the reaction mixtures after removal from the low temperature environment was generally observed. This is ascribed to the formation of conjugated oligomers of cyclohexene which are believed to be produced by the cationic attack of sulfuric acid on the cyclic unsaturated hydrocarbon. The sulfuric acid, in turn, is one of the reaction products of the heterolytic decomposition of t-butyl hydroperoxide in the presence of sulfur dioxide.<sup>82</sup>

The formation of cyclohexene oligomers was investigated by Sperling<sup>124</sup> who isolated both acid-insoluble saturated dimers and trimers (e.g., 1-cyclohexyl methyl cyclopentane) and acid-soluble unsaturated trimeric and tetrameric diolefins and high molecular weight polymer from the reaction of cyclohexene with 97% sulfuric acid. The increase in optical density at high temperatures is probably a consequence of this reaction, which also produces the methanol-soluble surface coloration of the polymer observed in the present investigation as well as in the investigation reported by Iwatsuki et al.<sup>87</sup>

Slopes of the linear portions of Figures 27 and 28 were obtained and are presented in Table XIII. The values of these slopes were converted to the rate constant expression applicable to the most probable polymerization mechanism, propagation by alternating addition and sulfonyl biradical termination. These values of  $(fk_d / k_{tSS})^{\frac{1}{2}} k_1 k_2 (k_{2R} + k_1 [S])^{-1}$  are listed in Table XIII and the logarithms of the slopes of the curves, (i.e., the rates of decrease of the logarithms of monomer concentrations), as well as the logarithms of the rate constant expressions are plotted against the reciprocal of the absolute reaction temperature in Figure 29.

The data plotted in Figure 29 show that a maximum reaction rate occurs at approximately  $-28^\circ\text{C}$ . At approximately the same temperature distinct changes in the polymer average molecular weight and molecular weight distribution were found to occur (Figure 14). A maximum reaction rate as a function of temperature must be caused by a reversible reaction. Because elemental reaction rate constants invariably increase with increasing temperature, a decrease in reaction rate with increasing temperature must be caused by a reaction which produces the reagent, i.e., a reverse reaction. The expected shapes of reaction-rate-temperature functions described by Dainton and Ivin<sup>90</sup> for propagation-depropagation polymerization reactions

TABLE XIII

Effect of Temperature on Rate Constants

Run Ident.	Temp., °C	[I] <sub>o</sub>	[S] <sub>o</sub>	[D] <sub>o</sub>	R <sub>OD</sub>	R <sub>S</sub>	1/Y <sub>OD</sub> x 1000	1/Y <sub>S</sub> x 1000	dR <sub>OD</sub> /dt	10 <sup>4</sup> [S] <sub>d</sub> k <sub>d</sub> , sec <sup>-1</sup>
64.01	-48.4±.2	0.046	0.658	3.282	0.884	0.82	0.493	0.549	0.432	0.127
61.05	-41.1±.4	0.046	0.685	3.732	1.128	1.11	0.604	0.713	0.857	0.252
61.06	-36.9±.2	0.046	0.666	3.294	1.735	1.78	0.968	1.195	0.856	0.252
61.03	-28.7±.1	0.046	0.663	3.270	4.208	3.72	2.40	2.55	1.60	0.471
61.04	-28.3±.1	0.047	0.665	3.401	6.133	4.22	3.34	2.74	2.79	0.822
56.09	-19.5±.5	0.045	0.655	3.173	2.93	-	1.86	-	3.54	1.043
51.01	-18.8±.4	0.045	0.670	3.355	2.29	3.60	1.36	2.57	2.82	0.831
61.01	-7.6±.1	0.045	0.635	3.135	-	2.32	-	2.86	5.52	1.626
61.02	-1.6±.3	0.045	0.644	3.240	-	1.10	-	8.23	17.64	5.197

## Remarks:

All concentrations in moles/liter

R<sub>OD</sub> = -100 x dlogOD/dt, min<sup>-1</sup> ; R<sub>S</sub> = -100 x dlog[S]/dt, min<sup>-1</sup>dR<sub>OD</sub>/dt = -100 x d<sup>2</sup>logOD/dt<sup>2</sup>, min<sup>-2</sup>

1/Y in liter/mol x sec defined in section III i 4

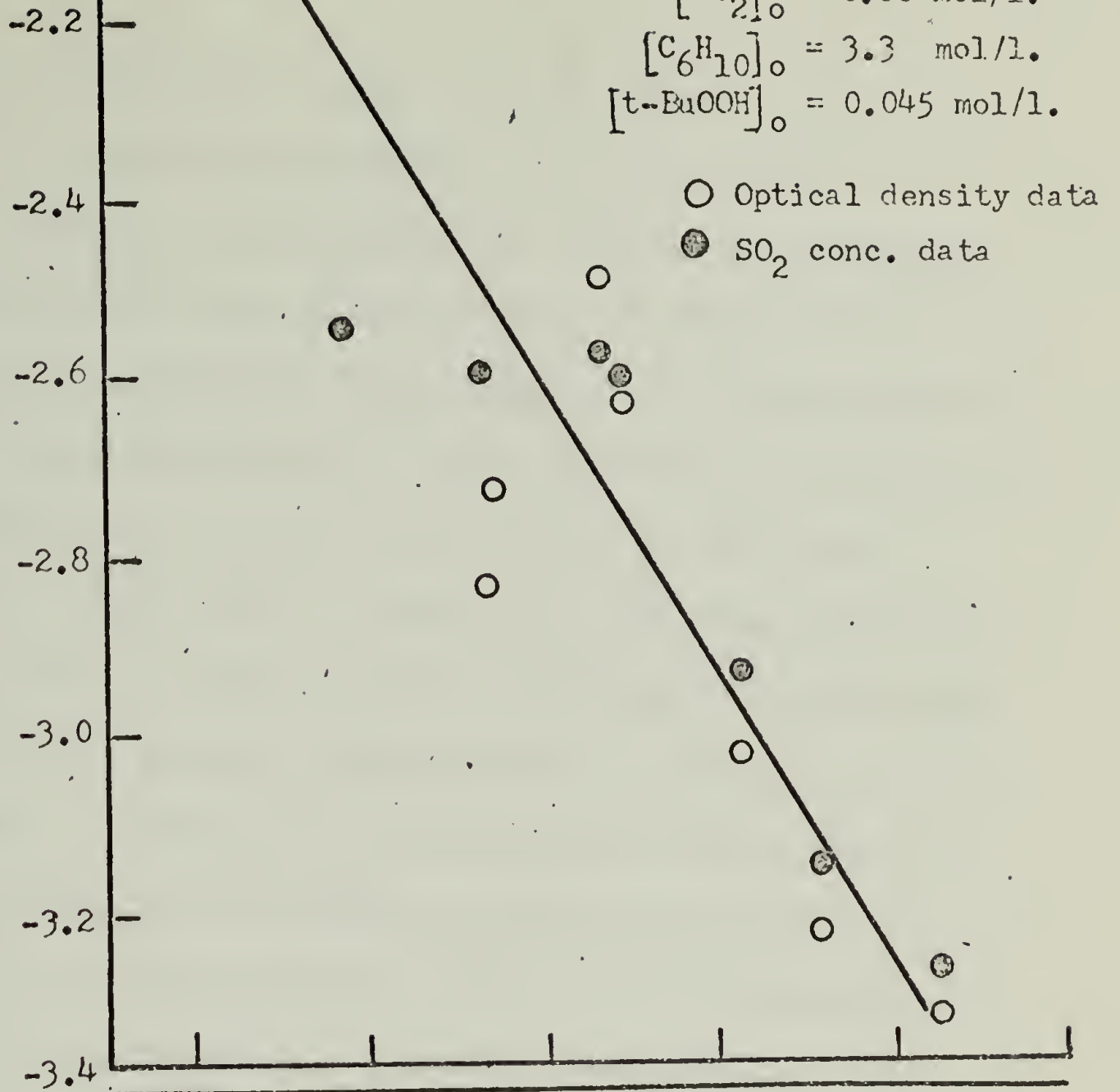
1/Y = (fk<sub>d</sub>/k<sub>tSS</sub>)<sup>1/2</sup>k<sub>1</sub>k<sub>2</sub>(k<sub>2R</sub>+k<sub>1</sub>[S]<sub>o</sub>)<sup>-1</sup>

Temperature range refers to time average standard deviation



$$\text{LOG}(1/Y) = \text{LOG}((fk_d/k_t)^{1/2} k_1 k_2 / (k_{2R} + k_1 [S]))$$

RECTIFIED REACTION RATE DATA



$$\text{LOG}(-d\text{LOG OD}/dt),$$

$$\text{LOG}(-d\text{LOG } SO_2/dt)$$

RATE OF MONOMER DISAPPEARANCE

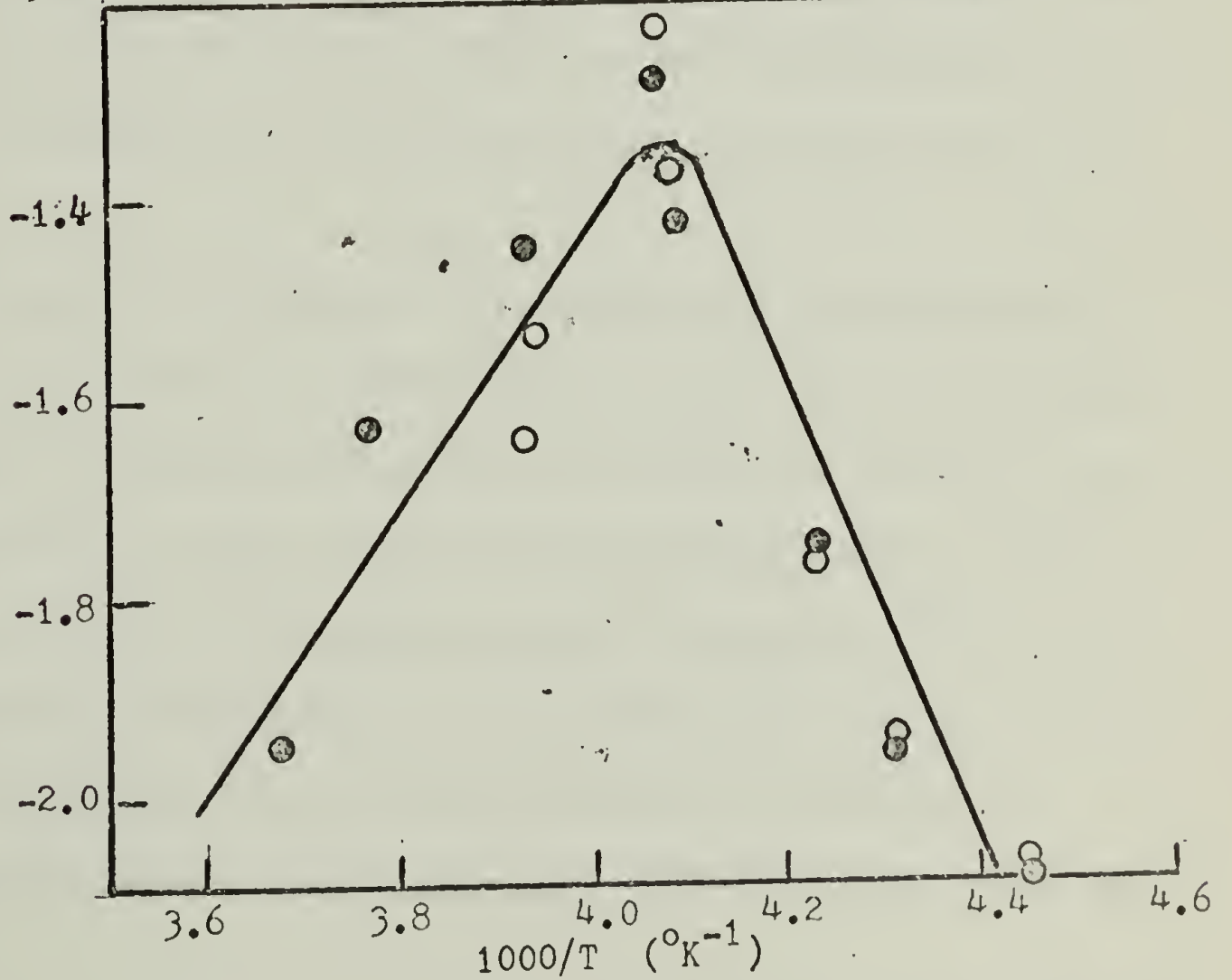


Figure 29. Effect of temperature on polymerization rate

conform to the general shape of the reaction rate curve presented in the lower portion of Figure 29.

The reaction rate constants plotted as a function of temperature in the upper portion of Figure 29 do not indicate the existence of a maximum. In the calculation of these constants from the reaction rates, the effect of depropagation was taken into account by the term  $([S][D] - [S]_e[D]_e)$ , where  $[S]_e[D]_e$  was estimated from the data of Cook, Dainton and Ivin.<sup>93</sup> Although scatter of the points in this plot is fairly great, due to the need to subtract an imprecisely known value of  $[S]_e[D]_e$  from the somewhat scattered rate data, no evidence of a maximum remains. The role of depropagation in the copolymerization of sulfur dioxide and cyclohexene is confirmed since a model which includes the effect of depropagation on the reaction rate rectifies the rate data.

Previous investigators have observed the phenomenon of decreasing overall polymerization rate with increasing temperature in copolymerization reactions of olefins with sulfur dioxide. They have attributed this effect either to propagation by the charge-transfer complex,<sup>57</sup> or propagation by both radical and cationic mechanisms,<sup>83</sup> or to a difference in the thermodynamic properties of polymer formed above and below the temperature of maximum

rate.<sup>47</sup> In the copolymerization of 1,3-cyclohexadiene with sulfur dioxide, Yamaguchi et al. found that the logarithm of the overall rate of polymerization increased approximately linearly with increasing reciprocal absolute temperature to a temperature of  $-35^{\circ}\text{C}$ , then decreased linearly with increasing  $1/T$ .<sup>47</sup> They determined the overall activation energy of the copolymerization from the low temperature portion of their curve to equal 4.7 kcal/mole. An investigation of the copolymerization of cyclopentene and sulfur dioxide carried out by Iwatsuki et al. revealed no anomalous rate-temperature relationship in the temperature region investigated,<sup>87</sup> and an activation energy of the overall polymerization process of 16.5 kcal/mole was observed.

The activation energy of the overall reaction between sulfur dioxide and cyclohexene, determined from the slope of the log reaction rate constant vs. reciprocal absolute temperature line of Figure 29, was found to equal approximately 8 kcal/mole.

The occurrence of significant depropagation should lead to a continuous decrease in polymer molecular weight and increase in the polydispersity as the temperature is increased. As discussed in section IIIh3, a discontinuous variation of these polymer properties was observed to occur at the approximate temperature at which the reaction



rate attained a maximum. A possible explanation presented to account for this observation postulates that although the depropagation rate constants are much less than the propagation rate constants (sect. IIIi4(a)) at temperatures above the temperature of maximum reaction rate, depropagation can still lead to a significant reduction in molecular weight.

The molecular weight data was obtained using samples obtained at the end of the polymerization which had been polymerized in the presence of a continuously decreasing monomer concentration. The effect of depropagation on the molecular weight distribution of polymer prepared while the concentration of monomer is decreasing is accentuated and depends to a large degree on the conversion. When depropagation plays only a small part, polymer prepared during the whole course of the polymerization will contain approximately the same small portion of low molecular weight entities. At temperatures when depropagation becomes significant, polymer prepared near the end of the reaction will contain more low molecular weight entities than that prepared at the beginning of the reaction. The term  $k_1 k_2 [S] [D] - k_{1R} k_{2R}$ , which describes the effective monomer concentration, decreases significantly as the monomer concentration decreases during the polymerization since the depropagation rate constants

are a significant fraction of the propagation rate constants. This might well result in a precipitous change in the polydispersity of samples prepared while the monomer concentration decreases at a temperature near the temperature at which a maximum reaction rate is observed.

#### IIIi7. Temperature effect in initiation reaction.

The variation of the slopes of the logarithm of the charge-transfer complex optical densities with time were determined for experiments conducted at constant reagent concentration and varying temperature (Figure 27). From plots of the logarithms of these slopes against time, similar to those presented in Figure 26 for the constant temperature experiments, values of the slopes of the lines, representing the negative second derivative of the logarithm of optical density with respect to time, were found. These values are presented in Table XIII. The pseudo-first order initiator decomposition rate constant,  $k_d [\bar{S}] = -2 d^2 \ln OD / dt^2$ , calculated from these slopes and converted to  $\text{sec}^{-1}$  by multiplying by  $(2.303/60)^2$  are presented in Table XIII and plotted against the reciprocal of absolute temperature in Figure 30. The data of Figure 30 can be expressed as the equation:

$$k_d [\bar{S}] = 2.1 \times 10^3 \exp(-8600/RT) \quad (3-61)$$

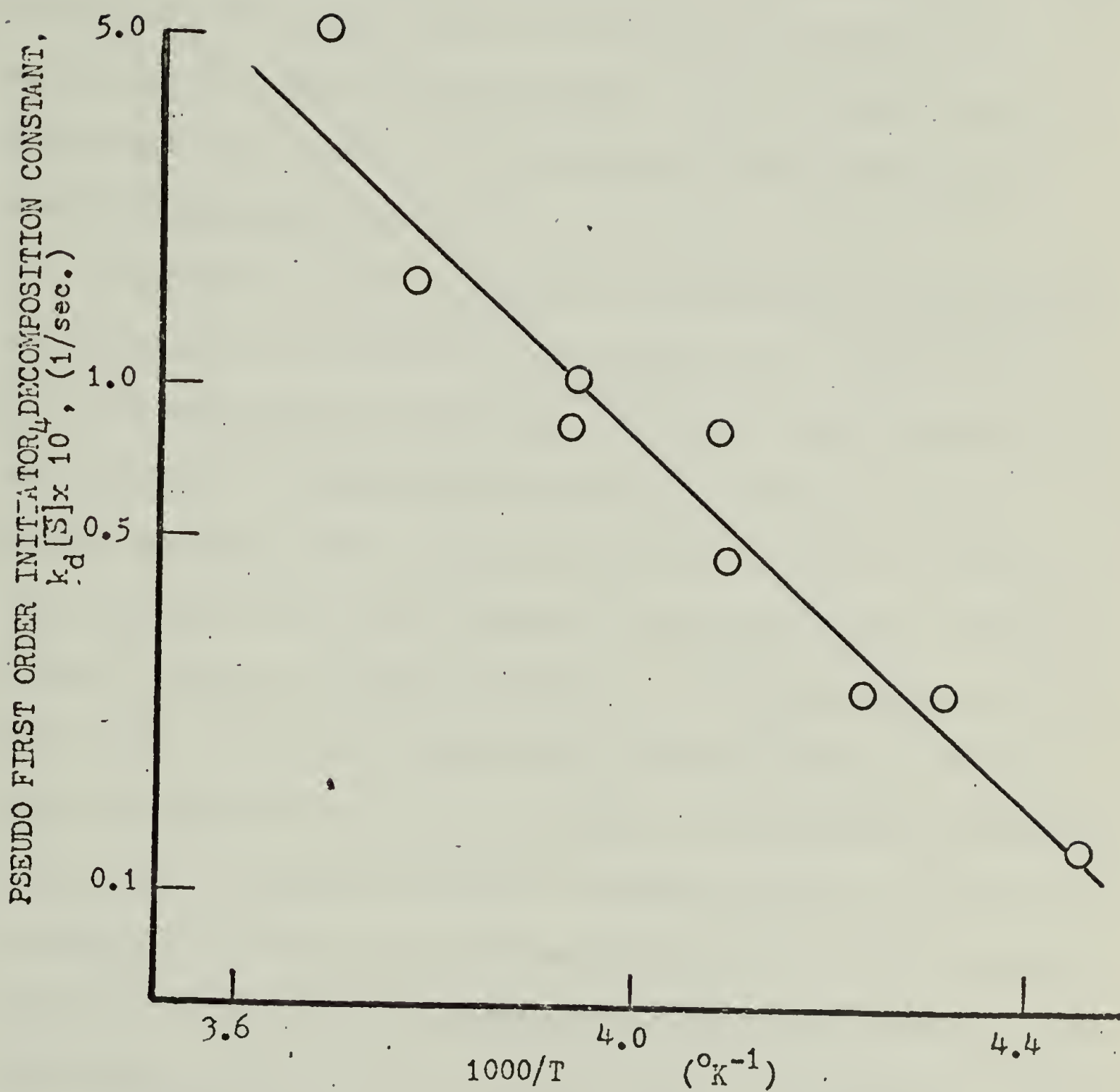


Figure 30. Evaluation of activation energy of the sulfur dioxide induced homolytic decomposition of t-butyl hydroperoxide



This equation removes 94% of the data variation. From the standard deviation of the slope of the line, the standard deviation of the initiator decomposition activation energy was found equal to 4.3 kcal/mole based on these data.

The low value of activation energy found for the initiator decomposition, 8.6 kcal/mole, is comparable to that determined for the ferrous ion-induced decomposition of substituted cumene hydroperoxides, which range from 12 kcal/mole for cumene hydroperoxide to 9.9 for t-butyl cumene hydroperoxide.<sup>125</sup>

A reduction in the energy of activation of peroxide decomposition is normally accompanied by a reduction in the pre-exponential collision frequency factor because of the structural modification of the transition state, which decreases the energy required to achieve reaction, also results in a more regular transition state configuration. Based on this increase in the entropy of activation with decreasing activation energy found in the induced decomposition of the cumene hydroperoxides referred to above, a frequency factor of approximately  $10^8$  should be found for the induced decomposition of t-butyl hydroperoxide. The low pre-exponential factor determined from these data for the pseudo-first order decomposition rate constant is assumed to be attributable to the low value of  $[S]$ , which is the effective sulfur dioxide concentration

required to induce the decomposition of t-butyl hydroperoxide. The investigation of Gosh and O'Driscoll,<sup>126</sup> in which the initiation of the polymerization of various monomers (e.g., methyl methacrylate, vinyl acetate and styrene) by t-butyl hydroperoxide was greatly enhanced by the addition of  $10^{-3}$  molar sulfur dioxide, is cited in support of this argument.

If the pre-exponential factor normally observed in the one-electron interchange induced decomposition of hydroperoxides is assumed to be applicable to the initiation reaction, the value of  $k_d$  at  $-19^\circ\text{C}$  equals approximately  $4.5 \text{ l mol}^{-1}\text{sec}^{-1}$ . The ratio of the propagation to the sulfonyl radical termination rate constants at this temperature,  $k_p/k_t^{1/2}$ , equals approximately  $0.64 \times 10^{-3} \text{ l mol}^{-1}\text{sec}^{-1}$ . Barb<sup>1</sup> found the value of  $k_p/k_t^{1/2}$  for the copolymerization of styrene and sulfur dioxide at  $20^\circ\text{C}$  to be  $0.62 \times 10^{-2} \text{ l mol}^{-1}\text{sec}^{-1}$ . Using Barb's values of the energy of activation of the propagation minus termination process,  $E_p - \frac{1}{2} E_t = 4.5 \text{ kcal/mole}$ , the value of  $k_p/k_t^{1/2}$  for styrene-sulfur dioxide copolymerization at  $-19^\circ\text{C}$  is extrapolated to  $1.8 \times 10^{-3} \text{ l mol}^{-1}\text{sec}^{-1}$ . In light of the approximations involved in comparing values of the constants, the three fold difference between the two values is probably not excessive. Increased resonance stabilization of the styryl radical compared to that of the

cyclohexyl radical should lead to a decreased value of  $k_p$  for the styrene copolymerization. The value of the activation energy of propagation minus that of termination,  $E_p - \frac{1}{2} E_t = E_o - \frac{1}{2} E_d$ , calculated from the activation energies of the overall polymerization reaction,  $E_o$ , and the initiator decomposition,  $E_d$ , determined in this investigation was found to equal 3.7 kcal/mole, in reasonable agreement with Barb's estimate of this activation energy in styrene-sulfur dioxide copolymerization.

IIIi8. Polymerization yield. Reaction conversions based upon both sulfur dioxide concentration (obtained from gas chromatographic analysis of the reaction mixture) and charge-transfer complex optical density (obtained from optical density data) are related to copolymer field (obtained by gravimetric analysis and calculated assuming equimolar copolymer formation) in Figure 31. The average yield was found to be  $3.5 \pm 6.5\%$  less than the conversion calculated from either the optical density or the sulfur dioxide concentration. The absence of a definite trend in the points indicates that the assumption of equimolar copolymer formation holds within the limits of experimental error. The small deviation of yield from conversion is an indication of the precision of the material balance (i.e., the amount of mechanical loss of copolymer in purification) because



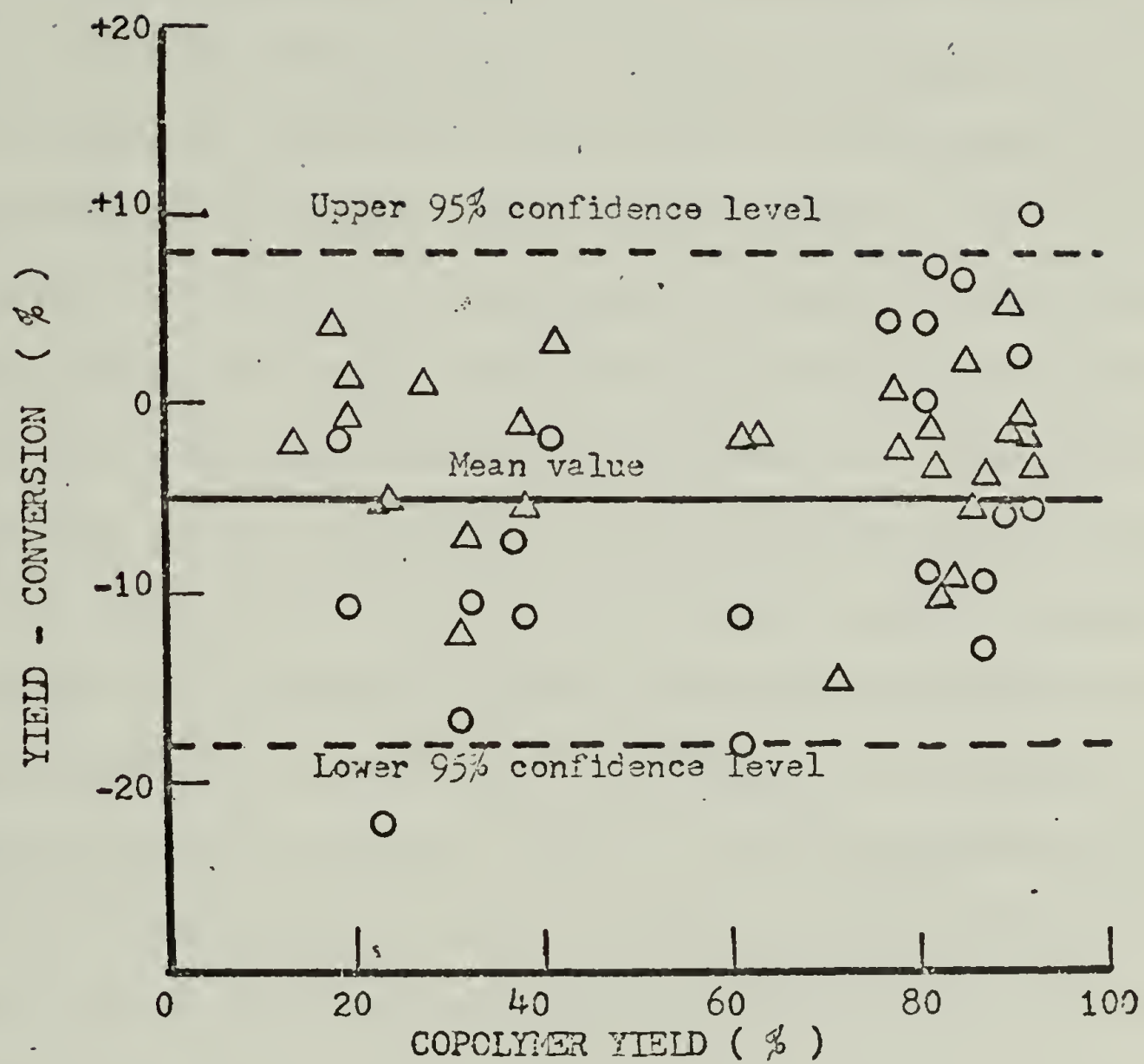


Figure 31. Copolymer yield

○ Conversion based on O.D. data  
 △ Conversion based on SO<sub>2</sub> data

no significant quantity of monomer is consumed in side reactions.

### IIIj. Heterolytic Decomposition of t-Butyl Hydroperoxide

The progress of the reaction between sulfur dioxide and t-butyl hydroperoxide in dichloromethane was followed in a manner similar to that used to investigate the polymerization reaction. The optical density and chromatographic concentration analyses of the reacting solution were obtained during experiments conducted at varying monomer concentrations and temperatures. The optical density of the solution at 360 nm (referred to the solution prior to the addition of t-butyl hydroperoxide) was observed to increase rapidly after the addition of the hydroperoxide, go through a maximum and decrease to an approximately constant value. Visual observation of this phenomenon revealed that a cloudy, light-scattering phase was formed upon addition of the hydroperoxide, but the small droplets of this phase coalesced as the reaction proceeded. After completion of the spectrophotometric studies (approximately 60 min. after injection of the hydroperoxide) the cuvettes contained a small volume of a yellow to brownish colored second phase of higher density than dichloromethane. The dichloromethane phase also

appeared somewhat yellow upon visual observation of the cuvette after removal from the spectrophotometer.

The sulfur dioxide concentration decreased very rapidly to a constant level and the concentration of a second component, eluting from the chromatograph 7 minutes after injection, remained substantially constant during the reaction. Typical curves relating optical density at 360 nm and the two chromatographically measured concentrations to time are presented in Figure 32. Although the chromatographic concentration determinations are quite scattered, the reaction appears to be very rapid, since the sulfur dioxide and second component concentrations remained substantially constant after the first 5-10 minutes of the reaction.

The initial, rapid increase in the solution optical density to a fairly distinct maximum value was followed by a decrease to a constant value and, at times, a subsequent increase in optical density. This behavior is attributed to the formation of a light scattering, second phase immediately upon addition of the hydroperoxide. The presence of the light scattering phase appears to cause a continual increase in optical density as long as formation of the second phase is taking place, after which the second phase continually coalesces, dropping out of the light path. Thus, the optical density probably



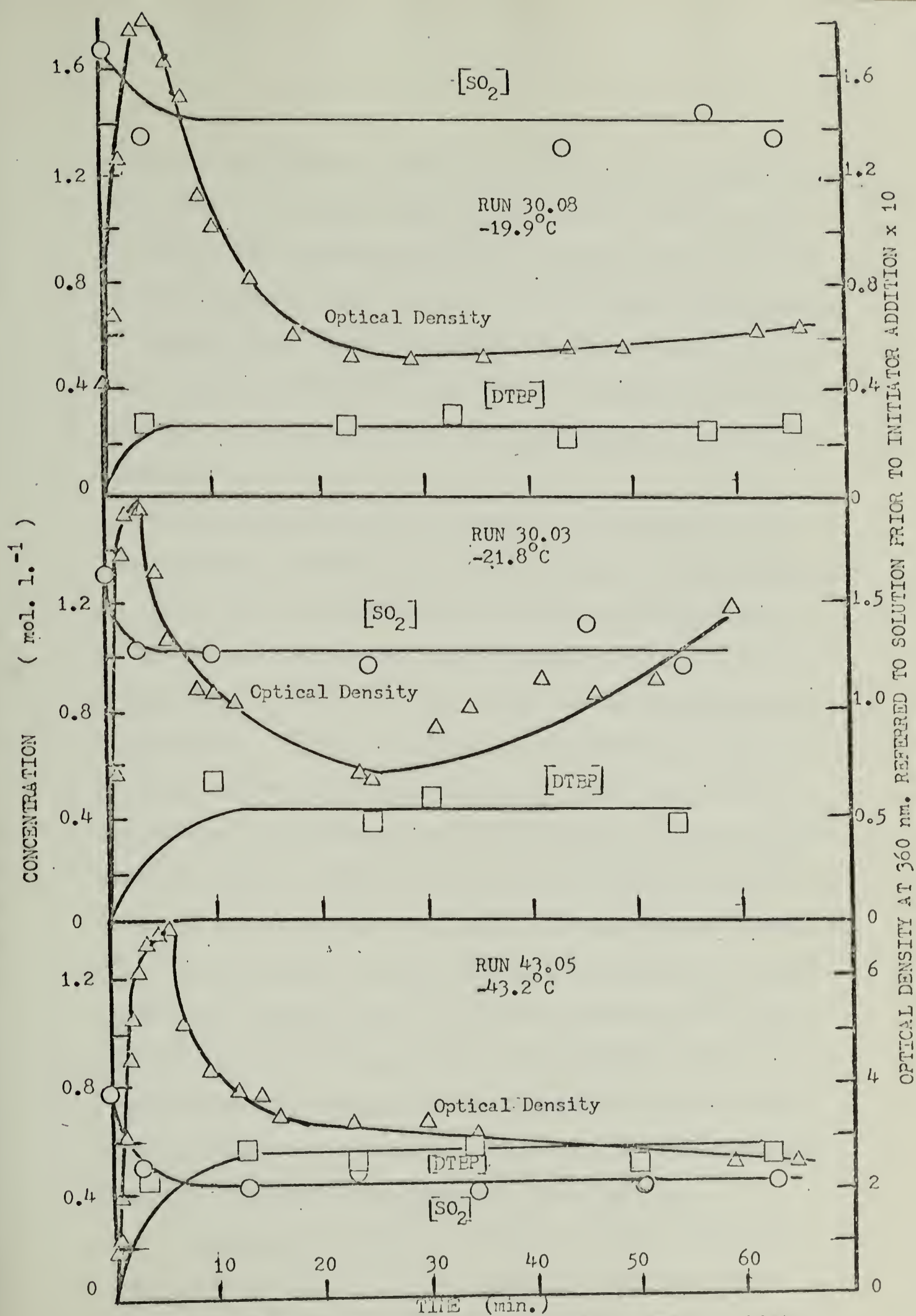


Figure 32. Heterolytic initiator decomposition reaction history

starts to decrease as soon as the reaction causing the formation of a second phase ceases. The observed approximate correspondence between the time of occurrence of the maximum optical density and the time of attainment of steady-state chromatographically determined concentrations appears to give credence to the hypothesis that the increase in optical density ceases when the reaction is complete.

It is interesting to speculate as to whether the "smoky region" observed by Zutty et al.,<sup>66</sup> and assigned to the locus of polymerization in the copolymerization of solid norbornene and sulfur dioxide vapor, is due to a phenomenon similar to that observed in the present investigation. In the experiment performed by Zutty, et al., the reaction rate appeared to be controlled by the rate of diffusion of sulfur dioxide through a sulfur dioxide swollen copolymer plug, and polymerization was observed to continue for 35 days. The reported formation of a "smoky region" and the physical conditions of the experiment suggest that a diffusion controlled sulfur dioxide-induced hydroperoxide decomposition initiation reaction may be a more likely explanation of the observations than the "spontaneous" initiation, "living free radical" hypothesis proposed by Zutty et al.

The second increase in optical density which was found to occur after 20-30 minutes is attributed to

formation of a colored product which caused the final solution to appear yellow or brown. This yellowing of the solution accelerated during venting and warming of the solution to room temperature. A possible explanation for the formation of chromophores in the reaction is the formation of trace quantities of unsaturated products from the decomposition of the hydroperoxide and subsequent cationically catalyzed oligomerization of these alkenes similar to the oligomerization of cyclohexene discussed in sect. IIIi5.

During these experiments it was observed that pressure in the cuvette increased when the t-butyl hydroperoxide was charged. This was indicated by expansion of the rubber serum cap. If the hydroperoxide was charged very rapidly, enough pressure was built up to blow off the serum cap in one experiment. Yellowing of the solution during addition of initiator was observed to take place if the initiator was added rapidly and to be absent if it was added slowly. These observations lead to the inferences that the reaction is highly exothermic and that the degree of color formation depends to a large degree on the temperature during the hydroperoxide charge which could be controlled only poorly due to the inability to remove heat of a rapid exothermic reaction from the cuvette.



IIIj1. Identification of reaction products, gas chromatography. Based on the elution time after injection, the reaction product observed in the gas chromatographic analysis may be di-t-butyl peroxide. Peak elution times of t-butyl hydroperoxide and some possible reaction products are listed below:

<u>Reagent</u>	<u>Time of elution of peak, min.</u>
t-butyl hydroperoxide	9
di-t-butyl peroxide	7
t-butanol	1.7
acetone	0.8
methanol	0.6

Infrared analysis. Infrared scans of capillary films between salt plates of the dichloromethane soluble and insoluble portions of one of the reaction products after evaporation of dichloromethane and sulfur dioxide but no other purification are presented in Figures 33 and 34. The following identification of the reaction products is based on these spectra. The dichloromethane insoluble fraction shows a strong absorption at  $1200\text{ cm}^{-1}$ , assigned to the  $\text{S} = \text{O}$  vibration in the  $\text{SO}_2\text{OH}^-$  structure, a broad hydroxyl absorption from  $3200$  to  $3500\text{ cm}^{-1}$  and very slight absorption due to C-H stretching at  $2900$  to  $3000\text{ cm}^{-1}$ . This phase was found to be highly acidic and to be denser than dichloromethane. These characteristics

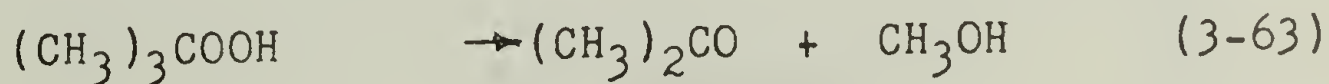
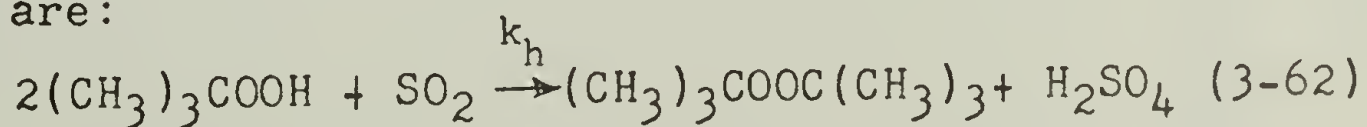
indicate that the dichloromethane-insoluble phase consists chiefly of a sulfur containing mineral acid, most probably  $\text{H}_2\text{SO}_4$ .

The infrared spectrum of the dichloromethane-soluble portion of the contents of the reaction cuvette shows a strong absorption at  $1260\text{ cm}^{-1}$  attributable to either a C-O stretching or O-H bending vibration, an absorption at  $1360\text{ cm}^{-1}$  characteristic of the C-H bending vibrations of t-butyl alkanes and a band at  $1710\text{ cm}^{-1}$  characteristic of the carbonyl stretching vibration of ketones. Some absorption in the  $3200 - 3500\text{ cm}^{-1}$  range due to hydroxyl stretching vibration is also present, although the absorption is not nearly as strong as the hydroxyl absorption of t-butyl hydroperoxide. The slight absorption band at  $890\text{ cm}^{-1}$  may be the absorption characteristic of the O-O stretching vibration of peroxides and hydroperoxides. From these band assignments it is inferred that the major dichloromethane-soluble reaction product is di-t-butyl peroxide and that a minor amount of a ketone, probably acetone is also present.

Nuclear magnetic resonance. The 60 MHz proton NMR spectrum of the unseparated, unpurified reaction product of sulfur dioxide and t-butyl hydroperoxide is presented in Figure 35. The sample was dispersed in  $\text{CDCl}_3$  but did not completely dissolve. The spectrum showed four major

singlet resonances. The chemical shifts from tetramethylsilane, assignments of the chemical shifts,<sup>127</sup> and the relative areas attributable to each of the absorptions are collected in Table XIV. This analysis confirms the presence of the  $\text{SO}_2\text{OH}$  group, probably as sulfuric acid, the presence of a significant amount of methyl protons with an electron donating group attached to the neighboring carbon atom, probably di-*t*-butyl peroxide, and shows that minor amounts of acetone and methanol are formed.

Evidence provided by these analytical methods show that the two major reaction products resulting from the reaction of sulfur dioxide and *t*-butyl hydroperoxide are sulfuric acid and di-*t*-butyl peroxide. These results are in accord with the results of Chien and Boss,<sup>82</sup> who attributed the formation of the major products to electrophilic addition to the hydroperoxide followed by C-C bond cleavage of the oxonium ion to form a carbonium ion, which adds to a second molecule of hydroperoxide. The formation of the products present in minor amounts, acetone and methanol, is ascribed to O-O bond cleavage of the oxonium ion. The overall reactions leading to the products are:





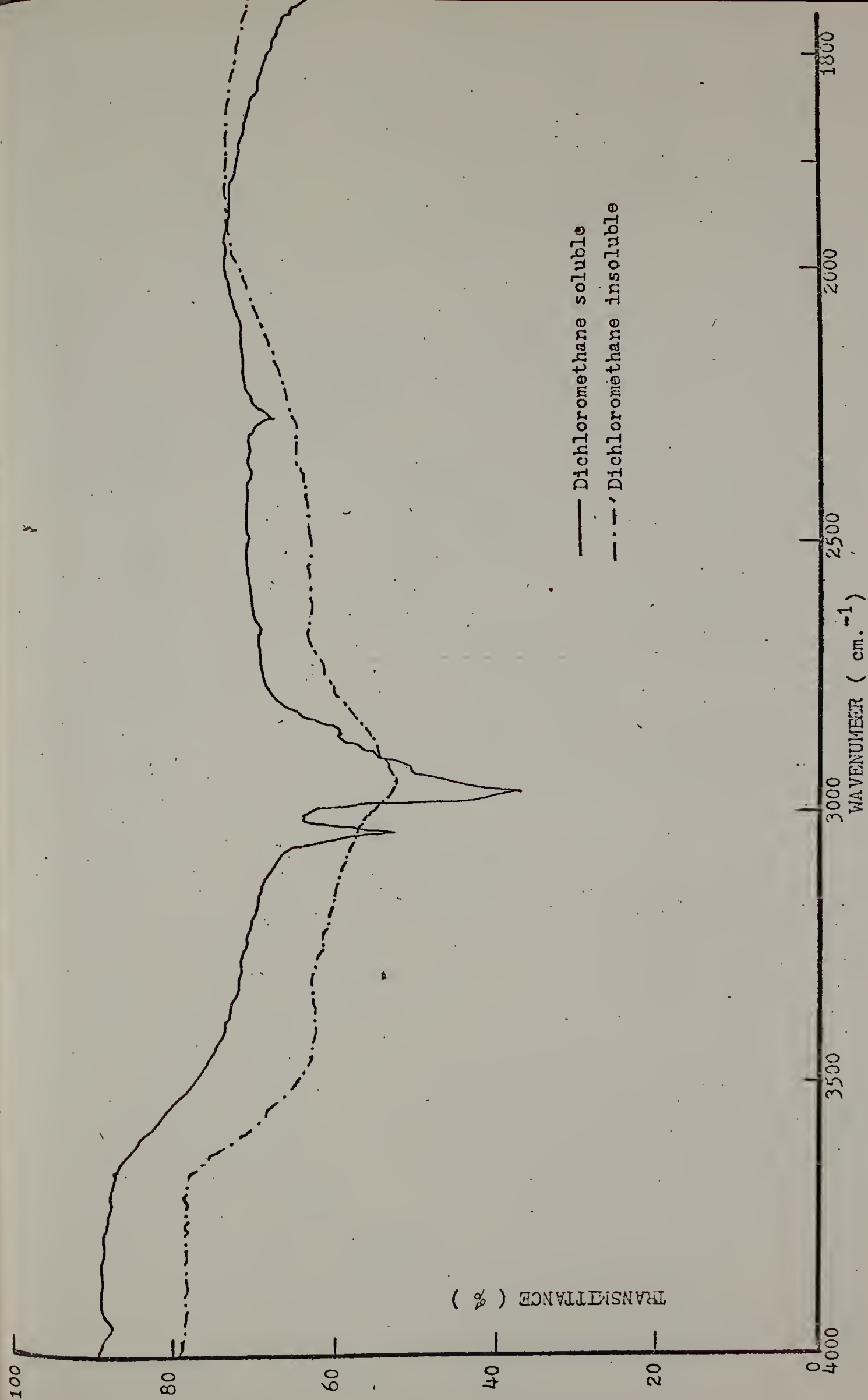


Figure 33. Infrared absorption spectra of the reaction products of sulfur dioxide and t-butyl hydroperoxide - high wavenumber region.

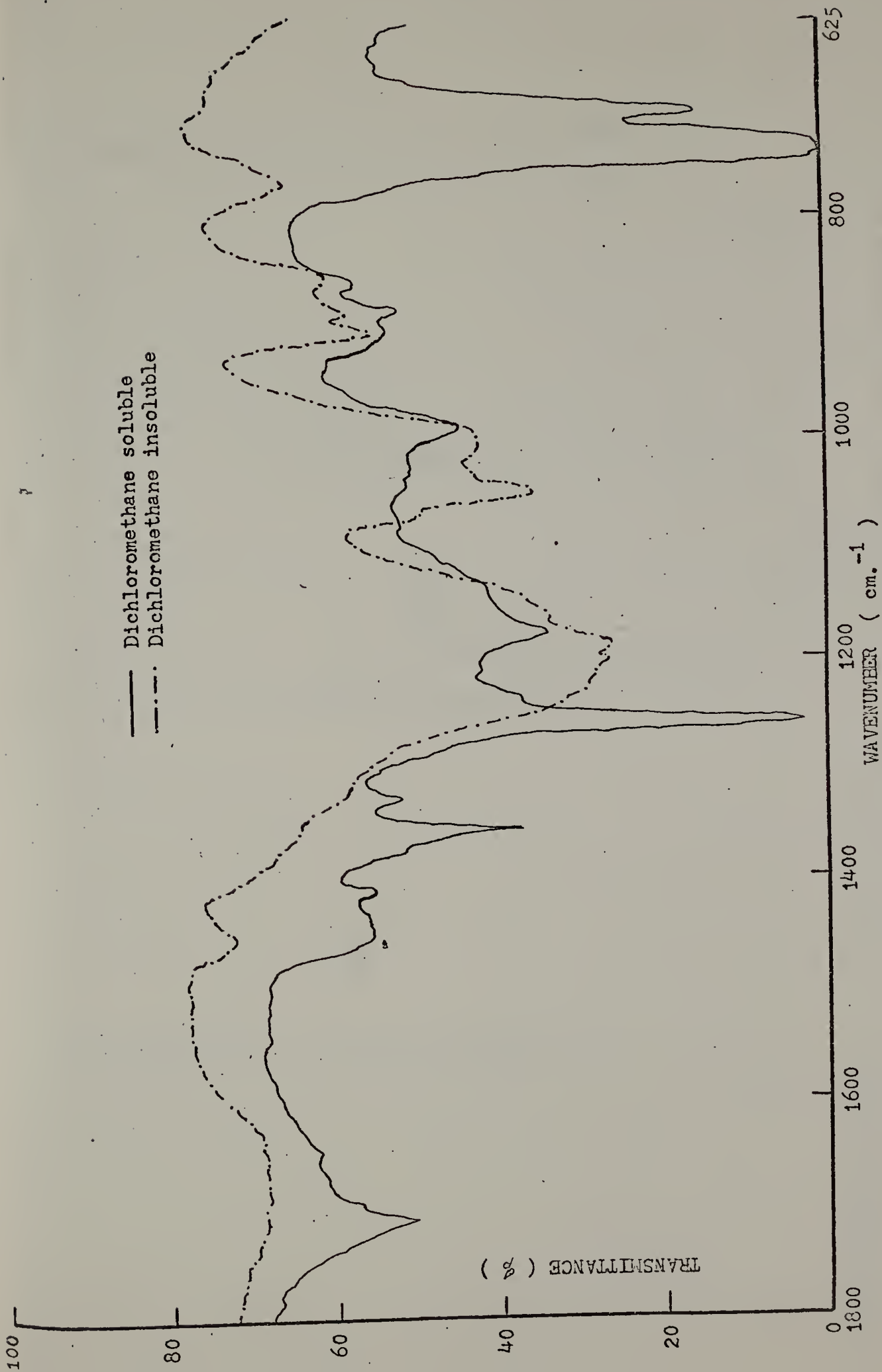


Figure 34. Infrared absorption spectra of the reaction products of sulfur dioxide and t-butyl hydroperoxide - low wavenumber region

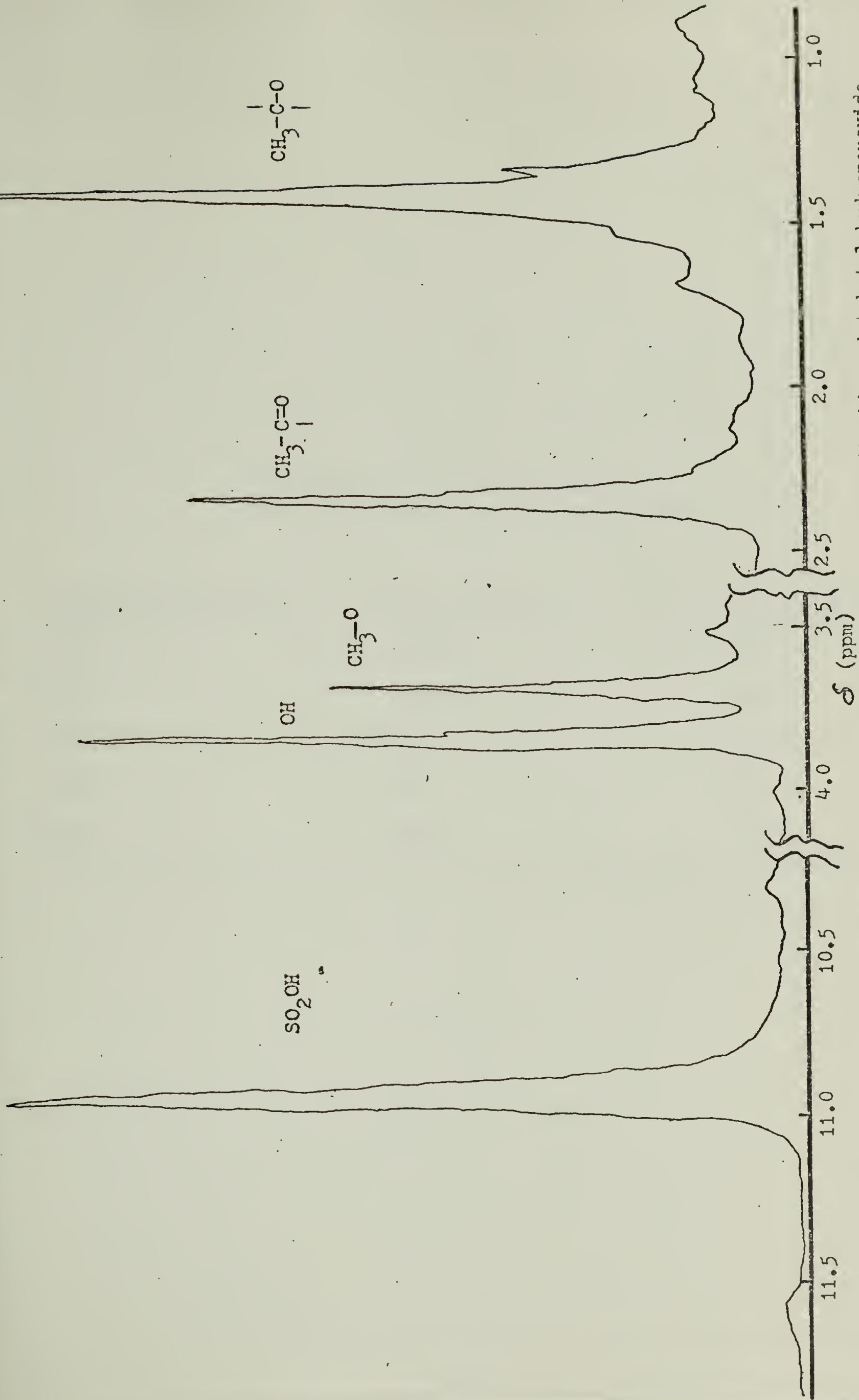


Figure 35. 60 MHz NMR spectrum of reaction product of sulfur dioxide and t-butyl hydroperoxide



TABLE XIV

NMR Analysis of Reaction Products of  
Sulfur Dioxide and t-Butyl Hydroperoxide

Chemical Shift, $\delta$ , ppm	Type of Proton	Relative Area
1.47	$\text{CH}_3-\overset{\textstyle  }{\underset{\textstyle  }{\text{C}}}-\text{O}$	0.267
2.40	$\text{CH}_3-\overset{\textstyle  }{\underset{\textstyle  }{\text{C}}}=\text{O}$	0.099
3.68	$\text{CH}_3-\text{O}$	0.058
3.82	OH	0.067
10.92	$\text{SO}_2\text{OH}$	0.509

IIIj2. Interpretation of kinetic data. The concentrations of the reagent, sulfur dioxide, and the product, di-t-butyl peroxide, at the end of the reaction were determined from the chromatographic analyses by averaging the values obtained in the steady-state period (Figure 32). These concentrations as well as the initial concentrations of sulfur dioxide are presented for experiments conducted at varying concentrations and temperatures in Table XV. The theoretical final concentration of di-t-butyl peroxide assuming complete conversion of the hydroperoxide to peroxide and the theoretical final sulfur dioxide concentration are also tabulated. Comparison of the experimental and theoretical values demonstrate that, within the limits of error of the data, the reaction goes to essentially complete conversion in a short time and that the reaction follows the stoichiometry of equation (3-62), which leads to the formation of the peroxide and sulfuric acid. The average percentage difference between theoretical and measured values,  $100 \times (\text{theory-measured}) / \text{theory}$ , was found to equal  $-4 \pm 11\%$  for the sulfur dioxide concentration and  $-22 \pm 29\%$  for the peroxide concentration.

Attempts made to arrive at a correlation of the optical density-vs.-time data proved unsuccessful. This is attributed to the fact that the optical density of the solution is affected by light scattering due to formation

TABLE XV

Initial and Final Reagent Concentrations and Evaluation of Rate Constant for Heterolytic Decomposition of t-Butyl Hydroperoxide

Run	Temp.,	[S] <sub>0</sub>	[I] <sub>0</sub>	<u>[S]<sub>∞</sub></u>		<u>[DTEP]<sub>∞</sub></u>		t <sub>max</sub> ,	k <sub>h</sub>
Ident.	°C			Found	Theory	Found	Theory	min.	
43.10	- 6.3	0.525	0.279	0.417	0.385	0.202	0.140	2.5	0.210
43.11	- 7.4	0.965	0.638	0.580	0.646	0.376	0.319	3.2	0.040
43.09	- 9.0	0.694	0.110	0.698	0.639	0.058	0.055	16.0	0.061
30.01	-19.2	1.687	0.126	1.511	1.624	-	0.063	8.0	0.040
56.08	-19.3	1.479	0.409	-	1.274	-	0.205	2.0	0.059
56.07	-19.4	1.545	0.485	-	1.302	-	0.242	6.2	0.016
30.08	-19.9	1.685	0.527	1.385	1.421	0.266	0.263	3.8	0.021
30.06	-20.3	1.904	0.723	1.566	1.542	0.376	0.361	4.2	0.013
30.04	-20.7	1.558	0.328	1.462	1.394	0.284	0.164	7.2	0.019
30.03	-21.8	1.316	0.835	1.020	0.898	0.441	0.417	2.8	0.026
43.01	-42.8	2.432	0.136	-	2.364	-	0.068	22.0	0.0093
43.06	-43.0	2.553	0.099	2.382	2.503	0.088	0.050	25.0	0.011
43.03	-43.1	1.985	0.765	1.762	1.602	0.306	0.382	4.2	0.011
43.05	-43.2	0.787	0.917	0.421	0.328	0.531	0.485	5.8	0.022
43.08	-46.7	2.063	0.161	1.858	1.982	0.104	0.080	13.2	0.016
43.07	-48.0	0.643	0.761	0.407	0.262	0.443	0.380	13.0	0.015

## Remarks:

All concentrations in moles/liter

DTBP = Di-t-butyl peroxide

t<sub>max</sub> = Time of occurrence of maximum optical density

k<sub>h</sub> refers to rate constant of heterolytic initiator decomposition in  
l<sup>2</sup>mol<sup>-2</sup>sec<sup>-1</sup>

∞ refers to steady state conditions at infinite time



of a second phase, droplet coalescence, yellowing of the solution due to the formation of trace amounts of conjugated olefins and to the decrease in sulfur dioxide concentration. It appears from Figure 32, however, that the time of occurrence of a maximum optical density coincides roughly with the time for the sulfur dioxide and di-*t*-butyl peroxide concentrations to reach steady-state values. If this time is assumed to be the time required to complete the reaction, a rough estimate of the overall heterolytic decomposition constant,  $k_h$ , may be obtained using the following approximation:

$$-\frac{\Delta [I]}{\Delta t} \approx \frac{[I]_0}{t_{\max}} \approx k_h [I]_{\text{av}}^2 [S]_{\text{av}} \approx k_h \left(\frac{[I]_0}{2}\right)^2 \left([S]_0 - \frac{[I]_0}{4}\right) \quad (3-64)$$

Values of the rate constant of the overall decomposition reaction calculated from the average sulfur dioxide and *t*-butyl hydroperoxide concentrations,  $[S]_{\text{av}}$  and  $[I]_{\text{av}}$ , and the time to reach a maximum in the solution optical density,  $t_{\max}$ , are presented in Table XV and the value of  $k_h$  calculated from equation (3-64) is plotted against the reciprocal of absolute temperature in Figure 36. The value of this third order rate constant of the overall decomposition reaction shows that the heterolytic decomposition of the hydroperoxide occurs at a faster rate than the homolytic decomposition ( $k_h = 0.02 \text{ l}^2\text{mol}^{-2}\text{sec}^{-1}$  vs.  $k_d [\bar{S}] = 0.9 \times 10^{-4} \text{ sec}^{-1}$  at  $-19^\circ\text{C}$ ), and that the overall heterolytic decomposition

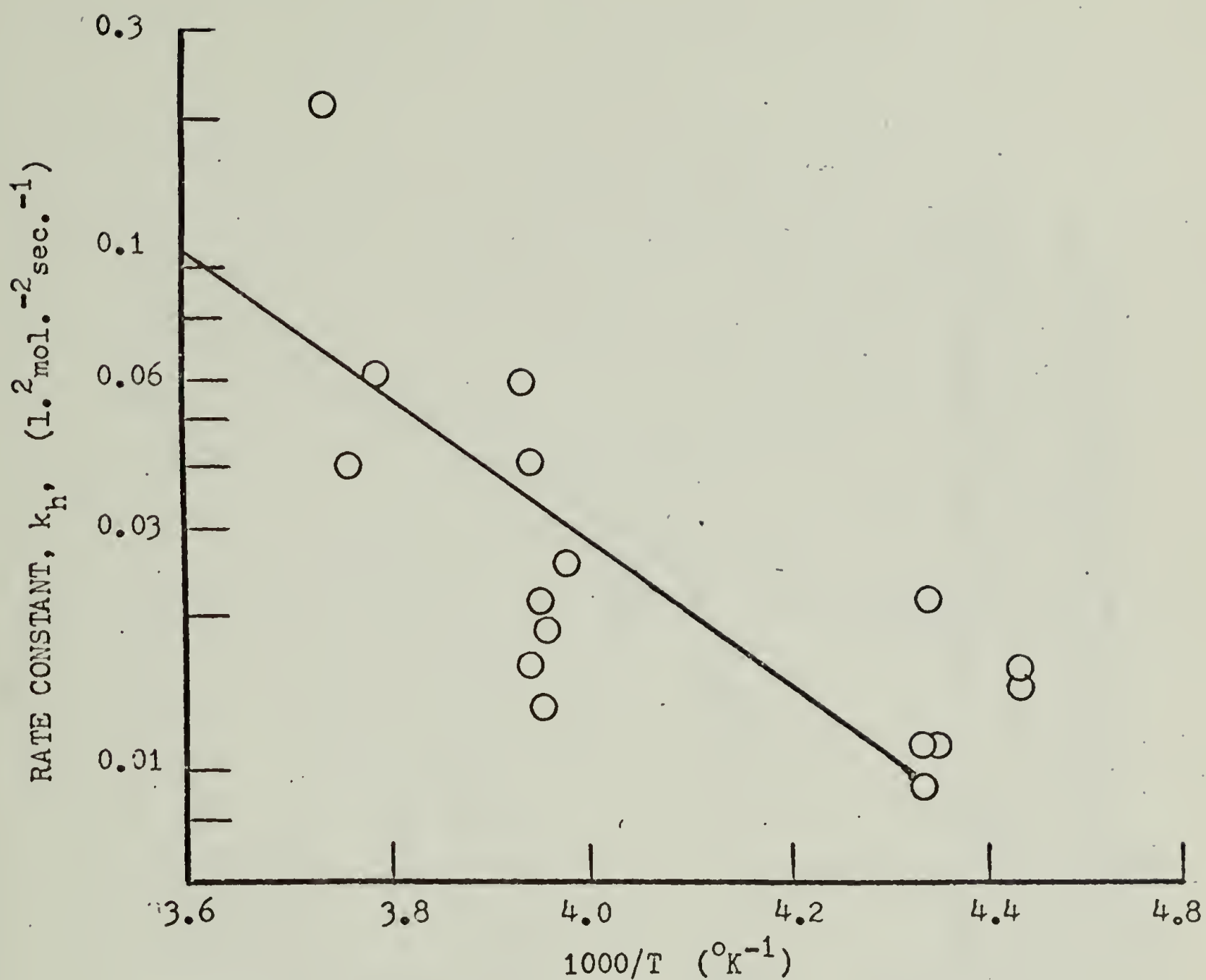
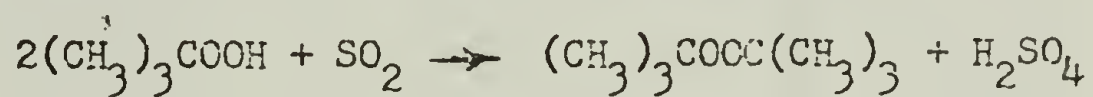


Figure 36. Rate constant for the overall heterolytic decomposition reaction of t-butyl hydroperoxide



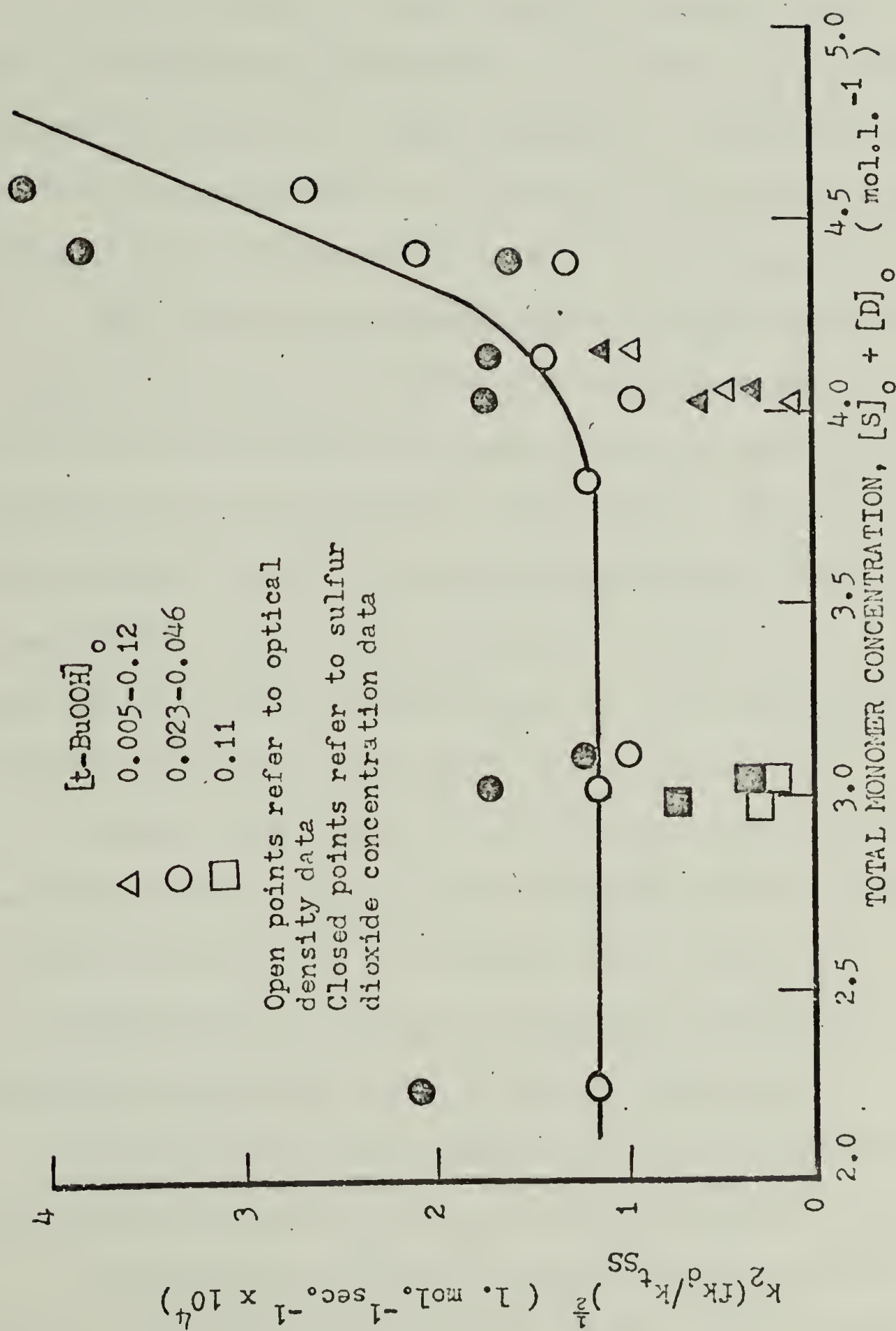


Figure 37. Effect of total monomer and initiator concentrations on the rate constants for alternating propagation and sulfonyl biradical termination



reaction has a low temperature coefficient (apparent activation energy  $6 \pm 2$  kcal/mole).

### IIIk. Summary

An equimolar charge-transfer complex formed from sulfur dioxide and cyclohexene was found to be present during copolymerization of these monomers. The spectrophotometrically determined concentration of this complex was observed to decrease during the polymerization reaction.

The equilibrium constant of complex formation, the complex extinction coefficient and thermodynamic properties were determined in n-hexane and compared with values found in the literature. The enthalpy of formation of the complex in dichloromethane was found to be significantly less than the enthalpy of formation in n-hexane and the extinction coefficient of the complex was significantly greater in the more polar solvent.

Within the limits of precision of the analytical methods used, the copolymers formed from the reaction of sulfur dioxide and cyclohexene were found to be composed of alternating, equimolar segments, independent of comonomer composition and reaction temperature.

Negligible chain transfer to chlorinated solvents was found to occur during the polymerization reaction.

Copolymers of 50,000 number average molecular weight and 1.6 polydispersity ratio,  $\bar{M}_w/\bar{M}_n$ , were prepared at

temperatures below  $-30 \pm 3^\circ\text{C}$ . The number average molecular weight decreased five fold and the polydispersity ratio increased by a factor of two when polymerization was carried out above this temperature. The change in molecular weight and distribution occurred over a very limited temperature range and negligible variation of molecular weight and distribution with temperature was found at temperatures above and below this range. The molecular weight dependence on initiator concentration was found to be less than the expected 0.5 power.

Initiation of the copolymerization did not occur spontaneously, i.e., without the addition of initiator, when purified cyclohexene was used. Spontaneous polymerization occurred, however, when the unpurified monomer was employed. Initiation of the copolymerization could be brought about by the addition of hydroperoxides, whereas peroxides and other initiators which have been reported to be effective in sulfur dioxide copolymerizations were not effective at the low experimental temperatures.

The hydroperoxide initiator was found to decompose both homolytically and heterolytically in the presence of sulfur dioxide. The heterolytic decomposition reaction produced a peroxide and sulfuric acid. The presence of sulfuric acid during the polymerization caused a surface coloration of the polymer presumed to be due to the

cationically catalyzed oligomerization of trace amounts of olefins. The occurrence of a heterolytic initiator decomposition reaction competing with the homolytic decomposition was found to cause the polymerization reaction to stop prior to the exhaustion of the comonomers.

Polymerization rate data was obtained from measurement of sulfur dioxide concentration and charge-transfer complex optical density. The reversibility of the propagation reaction was confirmed. The reaction rate data was found to fit a kinetic model based on propagation of the chain reaction by alternate addition of the two comonomers. A model assuming propagation by addition of the charge-transfer complex did not fit the data.

Based on the magnitude of the molecular weight distribution ratio,  $\bar{M}_w/\bar{M}_n$ , of polymers prepared at low temperatures, termination of the copolymer chain was determined to occur by combination rather than by disproportionation. A model in which it was assumed that combination of two sulfonyl radicals controls the termination reaction was found to fit the experimental data. If control of the termination reaction was assumed to take place by the combination of cyclohexyl radicals, the experimental data did not fit the assumed model. Insufficient data was available to permit evaluation of a model assuming control by the cross-termination reaction. Some



evidence was found for the diffusion control of the termination reaction.

From the fit of the experimental data to a sulfonyl radical control termination mechanism model, the inference was drawn that the sulfonyl radical concentration predominates. This led to the further inference that propagation is controlled by the addition of cyclohexene to the sulfonyl radical and depropagation of the sulfonyl radical.

Based on the relationship between polymerization rate and monomer concentration derived for the mechanism involving alternating addition propagation and sulfonyl biradical termination, the depropagation rate constants were found to be much less than those of propagation at  $-19^{\circ}\text{C}$ . However, the depropagation reaction becomes significant at this temperature at the low monomer concentrations existing at the end of the reaction. This phenomenon was invoked to explain the broad molecular weight distributions and low molecular weight of copolymer samples prepared at  $-19^{\circ}\text{C}$ .

Rate constants and activation energies of the polymerization and initiator decomposition reactions were determined. The most probable value of the combination of rate constants (for propagation by alternating comonomer addition and control of termination by combination of sulfonyl radicals),  $k_2(fk_d/k_{tSS})^{\frac{1}{2}}$ , was found to

equal  $0.0013 \pm 0.0002 \text{ l mol}^{-1} \text{ sec}^{-1}$  at  $-19^\circ\text{C}$ . The activation energy of the overall polymerization reaction was estimated to equal 8 kcal/mole. A pseudo-first order rate constant for the sulfur dioxide-induced homolytic decomposition of t-butyl hydroperoxide was found to equal  $0.9 \pm 0.2 \text{ sec}^{-1}$  at  $-19^\circ\text{C}$ . The activation energy of this decomposition reaction was evaluated to be  $8.6 \pm 4.3$  kcal/mole. Heterolytic decomposition of the initiator was found to proceed much more rapidly than the homolytic decomposition reaction. The heterolytic decomposition reaction was found to be only slightly temperature dependent.

### III.1. Conclusions

Based on the results of this investigation, the copolymerization of sulfur dioxide and cyclohexene initiated by t-butyl hydroperoxide proceeds according to the following mechanism.

Initiation reaction. The copolymerization is initiated by free radicals formed from the sulfur dioxide-induced homolytic decomposition of t-butyl hydroperoxide. A rapid heterolytic decomposition reaction of the hydroperoxide to produce sulfuric acid and di-t-butyl peroxide occurs in competition with the radical forming reaction. Due to this competing initiator decomposition

reaction, the free radical concentration decreases rapidly during the polymerization leading to cessation of the polymerization reaction prior to exhaustion of the monomers. The presence of sulfuric acid in the polymerization reaction results in a cationically initiated oligomerization of trace amounts of olefins, evidenced by color formation during the polymerization.

The ability of impure cyclohexene to initiate polymerization spontaneously confirms the conclusion of Sartori and Lundberg<sup>85</sup> that a previously reported spontaneous sulfur dioxide-olefin copolymerization<sup>66</sup> was actually initiated by a hydroperoxide impurity.

Propagation reaction. Chain propagation occurs by the reversible, alternating addition of sulfur dioxide to cyclohexyl radicals and cyclohexene to sulfonyl radicals. The rate controlling propagation step is the addition of cyclohexene to sulfonyl radicals and the depropagation rate is controlled by depropagation of sulfonyl radicals. The increasing importance of depropagation at high temperature leads to an increase in the molecular weight polydispersity and concomitant decrease in average molecular weight at high temperatures. A significant increase in molecular weight polydispersity was observed to occur over a narrow temperature range close to the temperature of occurrence of a maximum overall



polymerization rate. This observed discontinuity in the molecular weight temperature relationship is attributed to the combined effects of depropagation and decreasing monomer concentration during the course of the polymerization. Although the concentration of a charge-transfer complex formed from the comonomers decreases during the polymerizations, this complex does not act as the propagating species in the reaction.

Termination reaction. Termination occurs by the combination of free radicals rather than by their disproportionation. The predominant reaction leading to chain termination is the combination of two sulfonyl radicals.

With the exception of the discontinuities in the polymerization rate and molecular weight-vs.-temperature relationships at  $-30^{\circ}\text{C}$ , the phenomena reported in this investigation have been previously observed in sulfur dioxide-alkene copolymerizations and have been given varying interpretations. The data of previous investigators can, for the most part, be readily explained by the mechanism presented in this report. The major conclusion of this investigation, the non-involvement of the charge-transfer complex in the initiation and propagation steps, differs from the interpretation of the results by many investigators for alkene-sulfur dioxide copolymerizations.

Despite the non-involvement of the complex in the polymerization reaction, the spectrophotometric observation

of complex concentration during the reaction is an invaluable tool in the experimental determination of reaction kinetics.

### III. Recommendations

Confirmatory studies regarding the three principal conclusions emerging from this investigation should be undertaken. The principal difficulty in the interpretation of the experimental results of this study was in the confounding of the phenomena attributable to the polymerization initiation and propagation steps. This should be avoided in future studies by choosing initiation systems which do not interact strongly with monomers or solvents. The principal advantage of the present study over previously conducted investigations of polymerizations proceeding in the presence of charge-transfer complexes lies in the determination of the extent of the reaction by spectrophotometric observation of the charge-transfer complex concentration. This technique should be applied to future investigations of copolymerizations in which a readily observable charge-transfer complex is formed.

Role of charge-transfer complex. Additional studies of the role of the charge-transfer complex in copolymerizations of electron donor and acceptor monomers should be

undertaken to confirm the conclusions of this investigation. The experimental technique of spectrophotometric determination of charge-transfer complex concentration and chromatographic determination of monomer concentration during the polymerization should be used. The investigation of the alternating copolymerization of styrene and maleic anhydride initiated by benzoyl peroxide or azobisisobutyronitrile is recommended because this system is uncomplicated by reversibility effects or monomer interactions with initiator, possesses a readily observable ultra-violet charge-transfer absorption spectrum, is amply documented<sup>128</sup> and is of considerable commercial utility.

Effect of temperature on molecular weight and polymerization rate. Clarification of the mechanism which leads to the observed discontinuity of molecular weight distribution, which occurs close to the temperature at which a maximum overall polymerization rate takes place, should be undertaken. That study should also confirm or refute the explanation presented in the present work for the occurrence of a maximum polymerization rate observed in this and other sulfur dioxide-alkene copolymerizations. Work should be performed to determine whether a temperature dependent discontinuity in a thermodynamic property of the polymer (e.g., degree or type of crystallinity)



exists and to determine the effect of monomer concentration on molecular weight and molecular weight distribution. The solvent, comonomers and initiator used in this investigation should be used in the proposed study, which should consist of a detailed investigation of the effect of temperature and total monomer concentration on the reaction rate, molecular weight, copolymer composition and morphology of the polymer.

Initiation reaction. Further investigation of the effect of the sulfur dioxide-induced homolytic and heterolytic decomposition reactions on the free radical concentration and polymerization rate should be undertaken. This study should be carried out using an electron accepting monomer (e.g., acrylonitrile or methyl methacrylate) to preclude the formation of a sulfur dioxide-containing copolymer and should include an investigation of the effect of solvent on the reactions. Determination of the time dependence of free radical concentration using electron spin resonance techniques could provide a detailed description of the reaction mechanism.

In addition to these three major areas of investigation, future work should be performed to clarify the role of diffusion control of radical termination, to define the controlling termination mechanism with greater precision, to investigate possible solvent effects on chain propagation and to investigate further the effect of

initiator concentration on polymer molecular weight and distribution. These studies should be undertaken using the comonomers and initiator used in this investigation.

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## V. APPENDIX

## Va. Computer Program INCIN

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5*PRINT VALUES OF INITIAL AND FINAL CONCENTRATIONS OF COMPONENTS
6*IN KINETIC RUNS OF POLYSULFONE FORMATION
10 PROGRAM INCIN
11
20 DIMENSION V(20), CSO2(20), RSO2(20), CSOL(20), CHEX(20)
21X, RHEX(20), CTBH(20), RTBH(20)
23X, VORIG(30)
25 S=S2=0.0
30 READ, NREAD, VZERO, VSPAN
31 Z=NREAD
40 READ, SO2, SOL, HEX, TBH, POL
41 DO 45 N=1, NREAD
42 READ, VORIG(N)
43 S=S+VORIG(N)
44 S2=S2+VORIG(N)**2
45 CONTINUE
46 VREAD=S/Z
47 SD=SQRT((S2-S*VREAD)/(Z-1.))
50 VTEMP=VZERO+VREAD*VSPAN
60 T=.3451+26.453*VTEMP+.03592*VTEMP**2+.23825*VTEMP**3
70 CORR=.08414*(23.-T)
80 TCORR=T+CORR
85 TSD=25.3*VSPAN*SD
90
100 DS02=DENS(TCORR, -40., 1.509, 157.4)
110 DSOL=DENS(TCORR, 20., 1.3266, 236.2)
120 DHEX=DENS(TCORR, 20., .8102, 286.1)
130 DTBH=DENS(TCORR, 20., .896, 500.)
200 V(1)=SO2/DS02+SOL/DSOL
210 V(2)=V(1)+HEX/DHEX
220 V(3)=V(2)+TBH/DTBH
230 V(4)=V(3)-.1*POL
240 DO 280 N=1, 4
250 CSO2(N)=1000.*SO2/(64.06*V(N))
260 CSOL(N)=1000.*SOL/(84.93*V(N))
270 RSO2(N)=CSO2(N)/CSOL(N)
280 CONTINUE
300 DO 330 N=2, 4
310 CHEX(N)=1000.*HEX/(82.15*V(N))
320 RHEX(N)=CHEX(N)/CSOL(N)
330 CONTINUE
340 DO 370 N=3, 4
350 CTBH(N)=901.5*TBH/(90.12*V(N))
360 RTBH(N)=CTBH(N)/CSOL(N)
370 CONTINUE

```

```

380 CPOL=1000.*POL/(146.21*V(4))
390 RPOL= CPOL/ CSOL(4)
450 IF(CS02(4).LE.CHEX(4)) 460,470
460 YIELD=100.*CPOL/CS02(4);GO TO 500
470 YIELD=100.*CPOL/CHEX(4)
500 PRINT 510
510 FORMAT(*TOTAL VOLUME CONC. MOLAR RATIO TO SOLVENT*)
520 PRINT 530
530 FORMAT(*SULFUR DIOXIDE*)
540 DO 570 N=1,4
550 PRINT 560, V(N),CS02(N),RS02(N)
560 FORMAT(2F9.4,20X,F7.4)
570 CONTINUE
580 PRINT 590
590 FORMAT(*CYCLOHEXENE*)
600 DO 630 N=2,4
610 PRINT 620, V(N),CHEX(N), RHEX(N)
620 FORMAT(2F9.4,20X,F7.4)
630 CONTINUE
640 PRINT 650
650 FORMAT(*TERT. BUTYL HYDROPEROXIDE*)
660 DO 690 N=3,4
670 PRINT 680, V(N), CTBH(N), RTBH(N)
680 FORMAT(2F9.4,20X,F7.4)
690 CONTINUE
700 PRINT 710
710 FORMAT(*POLYMER*)
720 PRINT 730, V(4), CPOL, RPOL
730 FORMAT(2F9.4,20X,F7.4)
800 PRINT 805,YIELD
805 FORMAT(*YIELD = *,F6.2,* PERCENT*)
810 PRINT 815,TCORR,TSO
815 FORMAT(*TEMPERATURE = *,F6.2,* + OR - *,F6.2,* DEG. C*)
820 PRINT 830,CSOL(3)
830 FORMAT(*SOLVENT CONC. AFTER TBH CHARGE = *,F7.4)
900 END

1000 FUNCTION DENS(T,TSTD,RHOSTD, TC)
1010 TRSTD=(TSTD+273.15)/(TC+273.15)
1020 TR=(T+273.15)/(TC+273.15)
1030 WSTD=.1745-.0838*TRSTD
1040 W=.1745-.0838*TR
1050 DENS=RHOSTD*W/WSTD
1060 RETURN
1070 END
1080 ENDPRG

```

## Vb. Computer Program RAWDAT

```

5*PRINT OUT TABLE OF OPTICAL DENSITIES, TIMES AND WAVELEGTHS
6*FROM TRANSMITTANCE READINGS OF KINETIC RUNS
10 PROGRAM RAWDAT
20 DIMENSION LO(30), TO(30), ZO(30), KO(30), TIM(70), L(70),
21XT(70), Z(70), K(70), DIV(70), SP(70), ODO(30), AO(30), A(70)
22XOPT(10,50), ETBH(10), ES02(10), COR(10,50)
30 OD(T,Z,A)=.434295*LOG((T-Z)/A)
35 READ,C1,C2
40 READ,NPTS,LNO,CTBH,PL
45 PRINT 46
46 FORMAT(*TIME,MIN.   WAVELENGTH,MU   OPTICAL DENSITY*)
50 DO 80 J=1,LNO
60 READ,LO(J),TO(J),ZO(J),KO(J),ETBH(J),ES02(J)
80 CONTINUE
85 TIM(0)=0.0
90 DO 410 I=1,NPTS
100 READ,T(I),Z(I),K(I),DIV(I),SP(I)
101 L(I)=375
110 TIM(I)=TIM(I-1)+DIV(I)*SP(I)
120 DO 400 J=1,LNO
130 IF(L(I).EQ.LO(J)) 150, 400
150 GO TO (160,170,180,190) KO(J)
160 AO(J)=1.;GO TO 200
170 AO(J)=3.242;GO TO 200
180 AO(J)=11.78; GO TO 200
190 AO(J)=36.2; GO TO 200
200 ODO(J)=OD(TO(J),ZO(J),AO(J))
210 GO TO (220,230,240,250) K(I)
220 A(I)=1.;GO TO 260
230 A(I)=3.242; GO TO 260
240 A(I)=11.78; GO TO 260
250 A(I)=36.2
260 OPT(J,I)=ODO(J)-OD(T(I),Z(I),A(I))-ETBH(J)*PL*CTBH
265 COR(J,I)=OPT(J,I)+PL*ES02(J)*(C1-C2)
270 PRINT 280,TIM(I),L(I),COR(J,I)
280 FORMAT(F7.2,8X,I3,10X,F9.4)
400 CONTINUE
410 CONTINUE
420 END
430 ENDPROG
500
720

```



## Vc. Computer Program LINREG

```

10 PROGRAM LINREG
20 DIMENSION X(100),Y(100),YHAT(100),DEV(100)
21 DIMENSION TEMP(100),OD(100)
40 READ, N
46 Z=N
50 SX=SY=GX=P=.0
52 DO 55 I=1,N
53 READ,TEMP(I),OD(I)
54 X(I)=1./(1.987*(TEMP(I)+273.15))
55 Y(I)=LOG(OD(I))
56 DO 95 I=1,N
70 SX=SX+X(I);SY=SY+Y(I)
80 GX=GX+X(I)**2;GY=GY+Y(I)**2
90 P=P+X(I)*Y(I)
95 CONTINUE
100 XM=SX/Z;YM=SY/Z
110 DX=GX-XM*SX;DY=GY-YM*SY
120 DP=P-XM*SY
130 SL=DP/DX;TER=YM-SL*XM
140 RV=(DY-SL*DP)/(Z-2.)
145 RSD=SQRT(RV)
150 DS=SQRT(RV/DX)
155 T=ABSF(SL/DS)
160 DI=SQRT(RV*(1./(1./Z)+(XM**2/DX)))
170 R2=(SL**2)*(DX/DY)*100.
180 PRINT 181,SL,DS
181 FORMAT(*SLOPE=*,E12.5,*STD.DEVIATION OF SLOPE=*,E12.5)
182 PRINT 183,TER,DI
183 FORMAT(*INTERCEPT=*,E12.5,*STD. DEVIATION OF INTERCEPT=*,E12.5)
200 PRINT 201,R2
201 FORMAT(*PERCENT OF VARIANCE REMOVED=*,F10.4)
202 PRINT 203,T
203 FORMAT(*"T" OF SLOPE=*,F10.3)
204 PRINT 205,RSD
205 FORMAT(*RESIDUAL STD. DEVIATION=*,E12.5)
206 PRINT 207
207 FORMAT(*OBSERVED Y   CALCULATED Y   STD. DEV. OF POINT*)
210 DO 240 I=1,N
220 YHAT(I)=TER+SL*X(I)
230 DEV(I)=(YHAT(I)-Y(I))/RSD
235 PRINT 236,Y(I),YHAT(I),DEV(I)
236 FORMAT(2E12.5,F12.5)
238
240 CONTINUE
340 END
350 ENDPROG

```

```

10 PROGRAM GPC
20 DIMENSION CONC(100),COUNT(100),A(100),Z(100),ZM(100),
21X ZM2(100),ZM3(100)
30 READ,LIST,LSYM
35 MARK=0
40 READ,C1,C2,C3,C4
60 READ,Q,RUN
80 READ,COUNT0,DELT,N
90 COUNT(0)=COUNT0-DELT
100 READ,(CONC(I),I=1,N)
120 DO 400 I=1,N
140 COUNT(I)=COUNT(I-1)+DELT
160 A(I)=EXP(C1+C2*COUNT(I)+C3*COUNT(I)**2+C4*COUNT(I)**3)
180 Z(I)=CONC(I)/A(I)
200 ZM(I)=CONC(I)
220 ZM2(I)=CONC(I)*A(I)
240 ZM3(I)=CONC(I)*A(I)**2
300 SUMZ=SUMZ+Z(I)
320 SUMZM=SUMZM+ZM(I)
340 SUMZM2=SUMZM2+ZM2(I)
360 SUMZM3=SUMZM3+ZM3(I)

400 CONTINUE
420 V1=SUMZM/SUMZ
440 V2=SUMZM2/SUMZ
460 V3=SUMZM3/SUMZ
480 SIG2=V2-V1**2
500 SIG3=V3-3.*V1*V2-2.*V1**3
520 AN=V1
540 AW=V2/V1
560 RATIO=AW/AN
570 PRINT 575,RUN,Q
575 FORMAT(*RUN NO. *, F10.2,* " Q" FACTOR =*, F10.2)
580 PRINT 600
600 FORMAT(*      MOMENTS ABOUT ORIGIN                      JOMENTS ABOUT
601X MEAN*)
620 PRINT 640,V1
640 FORMAT(* FIRST*, 15X,E10.4,15X, *0.0*)
660 PRINT 660,V2,SIG2
680 FORMAT(*      SECOND*,15X,E10.4,15X,E10.4)
700 PRINT 720,V3,SIG3
720 FORMAT(*      THIRD*,15X,E10.4,15X,E10.4)
730 PRINT 740,AN,AW,RATIO
740 FORMAT(*AN= *,E10.4,* AW= *,E10.4,* AW/AN = *,F10.3)
780 PRINT 800,AN*Q,AW*Q
800 FORMAT(* MN = *,E10.4,* MW= *,E10.4)
820 PRINT 840,SUMZM
840 FORMAT(* SUM OF DATA POINTS, MM =*,G10.4)
860 IF(LIST.GT.0)870,950
870 CONTINUE
880 PRINT 900
900 FORMAT(*ELUTION VOL.      MOL. SIZE,A      W(M),Z      CUM.
901X WT. Z*)
920 DO 945 I=1,N
925 SC=SC+ZM(I)
930 SE=SE+ZM(I-1)
932 DE =SC-SE
935 PRINT 940,COUNT(I),A(I),100.*DE/SUMZM,100.*SC/SUMZM
940 FORMAT(F7.2,12X,G15.5,2F9.2)
945 CONTINUE
950 IF(MARK.EQ.0)960,1400
960 IF(LSYM.GT.0)980,1400
980 PRINT 1000
1000 FORMAT(* SYMMETRICAL DISTRIBUTION*)
1020 I=1; CONC(0)=0.
1040 IF(CONC(I).LT.CONC(I-1).AND.CONC(I).GT.5.)1060,1080
1060 M=I-1
1062 COUNT(I)=COUNT(M)
1065 GO TO 1100
1080 I=I+1
1090 GO TO 1040
1100 PRINT 1120,A(M)
1120 FORMAT(*MEDIAN MOL. SIZE,A. *,G15.5)
1140 DO 1200 I=1,N
1160 IF(I.GT.M)1180,1200
1180 CONC(I)=CONC(2*M-I)
1200 CONTINUE
1210 MARK=1
1220 SUMZ=SUMZM=SUMZM2=SUMZM3=0.0
1230 SC=SE=DE=0.
1235 N=2*M.
1240 GO TO 120
1400 END
1410 ENDPROG

```

## Ve. GLOSSARY OF SYMBOLS AND ABEREVIATIONS

A	Reaction component, electron acceptor
A	Preexponential collision frequency factor in Arrhenius equation
A	Sulfuric acid
$\bar{A}_n$	Number average polymer chain length
$A_p$	Preexponential collision frequency factor for propagation reaction
$A_r$	Preexponential collision frequency factor for depropagation reaction
AR	As received
$\bar{A}_w$	Weight average polymer chain length
B	Reaction component
C	Elution volume ( 5 ml counts)
C	Reaction component
C	Charge-transfer complex component of propagation reaction
C,C'	Combinations of polymerization reaction rate constants defined in section III i 4
c	Proportionality constant
D	Reaction component, electron donor
DMF	Dimethyl formamide
DTEP	Di-t-butyl peroxide
d	Differential operator
ESR	Electron spin resonance
$\Delta F^\circ$	Standard free energy change
f	Efficiency of utilization of radicals in polymerization reaction
GPC	Gel permeation chromatography



H	Di-t-butyl peroxide
$\Delta H^\circ$	Standard enthalpy change
$\Delta H^\ddagger$	Standard enthalpy of activation
$\Delta H_p$	Enthalpy change in polymerization reaction; Heat of polymerization
I	Intercept of line
I	Intensity of light transmitted through solution
I	Reaction component, initiator
$I_0$	Intensity of incident light
K	Equilibrium constant
$K_c$	Equilibrium constant of charge-transfer complex formation in terms of molar concentrations
k	Reaction rate constant
$k_1$	Rate constant for the addition of sulfur dioxide to an alkyl radical
$k_{1R}$	Rate constant for the depropagation of a sulfonyl radical
$k_{11}$	Rate constant for the addition of monomer 1 to radical 1
$k_{12}$	Rate constant for the addition of monomer 1 to radical 2
$k_2$	Rate constant for the addition of alkene to a sulfonyl radical
$k_{2R}$	Rate constant for the depropagation of an alkyl radical
$k_{21}$	Rate constant for addition of monomer 1 to radical 2
$k_{22}$	Rate constant for addition of monomer 2 to radical 2
$k_c$	Propagation rate constant for addition of alkene to chain
$k_d$	Rate constant of initiator homolytic decomposition
$k_h$	Rate constant of initiator heterolytic decomposition
$k_i$	Rate constant of initiation of polymerization
$k_p$	Rate constant of propagation reaction

$k_R$	Rate constant of depropagation reaction
$k_s$	Propagation rate constant for addition of sulfur dioxide to a chain
$k_t$	Rate constant of polymer chain termination reaction
$k_{tDD}$	Alkyl biradical termination rate constant
$k_{tSD}$	Crosstermination rate constant
$k_{tSS}$	Alkyl biradical termination rate constant
$l$	Optical path length
$\ln$	Natural logarithm
$\log$	Logarithm to base 10
$M$	Component of reaction, monomer
$\bar{M}_n$	Number average molecular weight
$\bar{M}_w$	Weight average molecular weight
$m$	Empirical constant in equation (1-22)
NMR	Nuclear magnetic resonance
$n$	Order of termination reaction
$n$	Molar ratio of components in a complex
$n$	Empirical constant in equation (1-22)
OD	Optical density
$\Delta OD$	Difference in optical density between a solution of a charge-transfer complex and a solution of light absorbing components in the absence of the complex
$OD'_a$	Optical density of sulfur dioxide solution at 290 nm; proportional to concentration of sulfur dioxide
$P$	Polymeric component of polymerization reaction
$\bar{P}$	Degree of polymerization
$P_{11}$	Probability of obtaining a two segment copolymer sequence consisting of two monomer 1 units

$P_{12}$	Probability of obtaining a two segment copolymer sequence consisting of a monomer 1 unit followed by a monomer 2 unit
$P_{AD}$	Fraction of acceptor molecules · uncomplexed
$Q$	Length of a polymer segment
$R$	Component of reaction, initiator fragment or growing radical chain
$R$	Gas constant
$R_i$	Rate of initiation of polymerization reaction
$R_p$	Rate of polymerization
$R_t$	Rate of chain termination
$r_1$	Copolymerization reactivity ratio, $k_{11}/k_{12}$
$r_2$	Copolymerization reactivity ratio, $k_{22}/k_{21}$
$S$	Reaction component, sulfur dioxide
$\Delta S^\circ$	Standard entropy change of complex formation
$\Delta S_p$	Entropy change in polymerization reaction
$\Delta S_p^\circ$	Standard entropy change of polymerization reaction
$\bar{S}$	Average sulfur dioxide concentration considered to be constant over a period of time
$s$	Slope of line
$T$	Absolute temperature, $^\circ K$
$T_c$	Ceiling temperature, $^\circ K$
TBH	t-Butyl hydroperoxide
THF	Tetrahydrofuran
$t$	time
$w$	Measured property of a charge-transfer complex
$X$	Component of reaction, charge-transfer complex
$x_D$	Mole fraction cyclohexene in cyclohexene-sulfur dioxide mixture



$Y_{OD}, Y'_{OD}$  Functions of reagent concentrations and rate of decrease of optical density used to evaluate rate constants of polymerization reaction; defined in section III i 4

$Y_S, Y'_S$  Functions of reagent concentrations and rate of decrease of sulfur dioxide concentration used to evaluate rate constants of polymerization reaction; defined in section III i 4

### Greek Symbols

$\Delta$  Finite change in property; positive value indicates an increase

$\delta$  NMR chemical shift parameter

$\delta_A$  NMR chemical shift of pure acceptor

$\delta_{AD}$  NMR chemical shift of charge-transfer complex

$\epsilon_a'$  Molar extinction coefficient of sulfur dioxide at 290 nm

$\epsilon_c$  Molar extinction coefficient of charge-transfer complex

$\Delta\epsilon$  Difference in extinction coefficients between complex and components of complex absorbing light at the wavelength of measurement

$\lambda$  Wavelength

$\rho$  Density

$\tau$  NMR chemical shift parameter;  $(10-\delta)$

### Subscripts

A Electron acceptor

Av Average conditions

C Charge-transfer complex

c Critical conditions

D Electron donor

e Equilibrium

n Chain length

- o Initial conditions
- r Reference conditions
- $\infty$  Infinite time

#### Superscripts

- Free radical
- o Standard state
- $\ddagger$  Standard state of activation

Numbers in run identification before period refer to notebook page numbers. Numbers after period refer to experiment number on this notebook page.



