THE CONTRIBUTION OF GAMMA RADIATION TO POLYMERIZATION OF STYRENE AT HIGH TEMPERATURES

THE CONTRIBUTION OF GAMMA RADIATION TO POLYMERIZATION OF STYRENE AT HIGH TEMPERATURE

by

MESBAH TAHERZADEH, B.Sc.(Chem. Eng.)

A Thesis
Submitted to the School of Graduate Studies
In Partial Fulfillment of the Requirements
For the Degree
Master of Engineering

McMaster University
March 1971

MASTER OF ENGINEERING (1971)
(CHEMICAL ENGINEERING)

McMASTER UNIVERSITY
HAMILTON, ONTARIO

TITLE: The Contribution of Gamma Radiation to Polymerization of Styrene at High Temperature

AUTHOR: Mesbah Taherzadeh, B.Sc.(Chem.Eng., Pahlavi University)

SUPERVISOR: Professor J.W. Hodgins

NUMBER OF PAGES: xv, 191

SCOPE AND CONTENTS:

The polymerization of styrene initiated with gamma radiation as well as thermal initiation was studied at temperatures, 150, 155, 160, 165, 180 and 200°C and dose rates of 0.072-0.1836 M Rads/hour. In all cases the reactions were studied up to 100% conversion and the following results were obtained.

(1) Rate of polymerization was independent of dose rate.

(2) 165°C was considered to be the temperature at which the radiation polymerization system in the case of styrene reaches a limiting rate of initiation caused by high temperature and dose rate.

(3) Self-production of ethynylbenzene in the system at 200°C probably caused retardation of the initial rate of polymerization.

(4) No significant gel effect was observed in the investigated temperature range.

(5) Polystyrene produced by radiation at high temperatures has a very low average molecular weight.

(6) A general mechanism was proposed based on the characteristics of the reactions.

(7) A temperature range was proposed as an optimal reaction temperature for radiation polymerization of styrene.

To My Daughter, AFSANEH

ACKNOWLEDGEMENTS

The author gratefully acknowledges the encouragement, advice and excellent guidance of Dr. J.W. Hodgins through all phases of this research. In addition, the suggestions offered by him while this thesis was being prepared were greatly appreciated.

He is particularly indebted to Dr. A.E. Hamielec for his guidance in this study as well as Dr. S.P. Sood of the University of Hawaii and Dr. Z. Horak of the Synthetic Rubber Research Institute in Czechoslovakia for their valuable advice and discussions. Special thanks are extended to S.T. Balke, without whose generous assistance, the G.P.C. portion of this work would not have been possible.

Included in the acknowledgements, the author would like to thank Dr. A.W.T. Hui for his helpful discussion, Mr. J. McDougall, atomic reactor superintendent, for his help during the repair of hot cell equipment and Mrs. Pat Meadowcroft for her careful and conscientious work in typing this dissertation. Thanks also to Polymer Corporation, Sarnia for their G.P.C. Analysis of samples and for provision of styrene monomer, and the Department of Chemical Engineering, McMaster University, for providing financial assistance in the form of scholarships.

Finally, to my wife, Homa, for her patience, and forbearance, and for providing a haven in which to forget the cares of graduate life.

TABLE OF CONTENTS

APPENDICES

APPENDICES PAGE

APPENDICES PAGE

NOMENCLATURE

A	Absorbance
a	Absorbancy Coefficient
b	Thickness of the Medium
c	Concentration of the Solute
D_A	Dose Rate in System A
E	Overall Activation Energy
E_i	Initiation Activation Energy
E_p	Propagation Activation Energy
E_t	Termination Activation Energy
e.V.	Electron Volt
$G^\bullet_M$	G Value for Monomer Free Radical Production
$G^\bullet_P$	G Value for Polymer Free Radical Production
g	Gram
G.P.C.	Gel Permeation Chromatography
I	Dose Rate (Discussion of the Results Section)
I	Intensity of Light Transmitted Through the System
I_0	Intensity of Light Falling Upon the System
K_{oo}	Recombination of Primary Free Radicals Rate Constant
K_{po}	Rate Constant for Addition of Free Radical to Monomer
K_p	Propagation Rate Constant
K_t	Termination (Combination or disproportionation) Rate Constant
K_{to}	Termination by Free Radical Rate Constant
M.W.D.	Molecular Weight Distribution

M.e.V.	Million Electron Volts
M	Mole
$\bar{M}_W$	Weight Average Molecular Weight
$\bar{M}_n$	Number Average Molecular Weight
ML	Milli liter
$m\mu$	Millimicron
M	Monomer
[M]	Monomer Concentration
N	Normality
O.D.	Optical Density
O.D.	Outside Diameter
P	Pressure, mm Hg
$\bar{P}_n$	Degree of Polymerization
P_n	Dead Polymer
R_p	Overall Reaction Rate
$R^\bullet$	Primary Free Radical in General
R_i	Rate of Initiation
$RM^\bullet$	Free Radical of any Chain Length
$[R^\bullet]$	Total Free Radical Concentration
$[RM^\bullet]$	Free Radical of any Chain Length Concentration
T.+R.	Thermal + Radiation
T.	Thermal
T	Transmittance
t	Temperature °C

T.H.F.	Tetrahydrofuran
μ/ρ	Mass Energy Absorption Coefficient
$\phi_M[M]$	Rate of Monomer Free Radical Production in Moles per Liter per Unit Radiation Dose

LIST OF FIGURES

FIGURE NUMBER PAGE

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Styrene is the trade name of the versatile chemical vinyl benzene. The reactivity of styrene monomer and its generally desirable properties, availability at low price and ease of handling, have resulted in a variety of uses being found for the monomer. The wide applicability of its polymer, polystyrene, has generated a good deal of research into the reaction characteristics of the monomer, method of production of the polymer and modification of polymer properties. The stimulus given to styrene production by the synthetic rubber program led to the installation of large scale, efficient, processing equipment, establishing styrene monomer as one of the most available low-priced industrial chemicals. Some of the uses of styrene are:

1) Production of synthetic rubber,
2) Production of polystyrene,
3) Copolymerization of styrene with other monomers,
4) Formulation of protective coatings,
5) As a casting and impregnating material,
6) As a modifying additive for laminating and casting resins,
7) As a chemical intermediate, and
8) As an aromatic.

The total production of styrene monomer in 1969 of the U.S. chemical companies (1) amounted to approximately 13,200,000,000 pounds.

By far, the largest amount of styrene produced was utilized in the production of synthetic rubber. The total production of polystyrene in 1969 was about (1) 7,200,000,000 pounds (in the U.S.A.). The total production figures for styrene and polystyrene in 1970 are nearly 1.2 times the 1969 production (2).

The increase in the production of styrene and polystyrene produced over the past two decades (1949 production figures (8) are Styrene 391,000,000 pounds, polystyrene 203,486,014 pounds) which is nearly 40 times the total production in 1949 is indicative of the remarkable degree of market acceptance of the material. The increase in plant facilities for producing styrene and polystyrene that are in the process of construction or announced by chemical industries (69, 12, 13) is tangible evidence of the long range confidence in the potentialities of these products. Dr. John Grebe of the Dow Chemical Company has called polystyrene the "cast iron" of the plastic industry. Like cast iron it is cheap, plentiful and satisfactory in a wide variety of applications. However, it possesses, like all materials, certain limitations which are inherent in its physical structure. The most significant factor influencing the physical structure of polymers is the technique of production. There are a number of polymerization methods which can be readily employed for the conversion of styrene and styrene mixtures to their corresponding polymers. The exact method to be used for polymerization will be dictated in part by the scale of operations and in part by the intended use of the polymer. There are four conventional polymerization techniques. Batch or

continuous mass polymerization uses pure styrene monomer, in solution polymerization styrene monomer diluted with solvent is used.
The suspension and emulsion polymerization techniques use water as a carrier along with a stabilizing agent such as starch to keep the material in suspension in the former, and in the latter an emulsifying agent to give extremely small particles.

Each of these methods has its advantages and disadvantages. A detailed discussion of these methods is available in (67).

Not only is the technique of production important in determining physical properties, but the rate of polymerization also influences the physical characteristics. It is well known that the polymerization rate of styrene can be accelerated considerably by the use of various catalysts such as light, metallic halides, organic peroxides, ozonides, pre-acids and other compounds which decompose readily to form free radicals. Heat and γ radiation are two other means of increasing the rate of polymerization. A similarity can be noted in the effects of temperature and catalyst upon the polymerization reaction since an increase in either of them will result in an increased rate, and a lowering of the molecular weight of the polymer formed. Catalysts offer certain advantages in bulk polymerizations from the stand-point of control of the exothermic reaction and reduction of the volatile material in the finished polymer. Polymerization reaction proceeds rapidly at the start, it slows down when the solid state is reached, so after it is 90% complete the 10% remaining polymerization proceeds at slow rate. This has an important bearing on the final product, since any unpolymerized monomer remaining in the polymer has a detrimental effect on optical properties, flow characteristics, chemical stability, electrical properties; it also reduces its heat distortion temperature because the remaining monomer acts to plasticize the polymer and what is more disturbing, it eventually produces blushing and crazing of the sample through evaporation of the monomer. Finally, it promotes discolouration of the product at elevated temperatures and in the sunlight because of the sensitivity of the remaining monomer to oxygen, also the presence of more than 0.1% of monomer in the final product is prohibited, if the finished product is to be used for food packaging because styrene monomer is a toxic substance (62, 8, 10).

Rubens et al (67) have shown the slowness of the final polymerization stage by showing the analytical data for a series of samples polymerized for as long as 60 days at 125°C. The volatile content (by vacuum extraction) levels off at about 1% while the monomer content (determined by U.V. absorption) levels off around 0.5%. In general, it is impractical to continue a polymerization for such long periods of time, and fortunately a brief finishing treatment at a high temperature is equivalent to a much longer period at a low temperature.

The design of the polymerization reactor is the ultimate objective of our group. This group is divided into two sub-groups. The work of the first sub-group is concerned with thermal polymerization kinetics and reactor modelling.

Studies of the second sub-group are mainly involved with the investigation of the use of gamma radiation as an initiator for the polymerization of vinyl monomers, such as styrene and methyl-methacrylate. The first study of gamma induced polymerization of styrene in this group was conducted by Dean (14). He studied the gamma-initiated polymerization of commercial styrene. Conversions up to 50% were obtained and the molecular weight distribution, intrinsic viscosity, bulk viscosity and osmotic pressure of several samples were measured and a theoretical kinetic model was developed (14). The post irradiation annealing of a highly converted styrene-polystyrene system was investigated by Elaraby (15) of this group. He also studied the experimental conditions necessary for the entrapment of a high concentration of free radicals. These conditions were found to bear a relation to the glass transition temperature of the system. The free radicals decay was examined at varied temperatures above and below glass transition temperatures (15). A comprehensive study of the radiation induced polymerization of styrene at a series of temperatures above ambient and at several dose rates was carried out by Sood (16). In all cases reactions were studied up to 100% conversion with the objective of developing kinetic models for the polymerization of styrene at high conversions. Close examination of the early stages of polymerization has led to the following conclusions:

1) There exists a critical temperature (109°C) above which the rate of polymerization is independent of dose rate, over a wide range of gamma intensities (about 16-fold).

2) This dose rate independence is ascribed to a limiting rate of initiations, characteristic of the intensity range.
3) A consequence of this is that at a given temperature above the critical temperature the degree of polymerization is also dose rate independent.
4) The above phenomena can be expected in any vinyl monomer, where the monomer is fairly active, and produces relatively stable radicals (16).

In undertaking the present study the following reasons were considered:

A) In the first phase we wanted to see whether dose rate independence after 109°C persists up to 200°C.
B) Secondly, we wanted to see whether the radiation initiation contributes to the rate of polymerization as the thermal reaction becomes increasingly significant.
C) To get a preliminary idea of the physical nature of the product, e.g., M_W.
D) To find a temperature at which conversion rate is optimal consistent with 100% conversion.

High energy gamma radiation was selected as the polymerization initiator and the experiments were carried out at temperatures 150, 155, 160, 165, 180 and 200°C. In most cases the reactions were carried out up to 100% conversion. All of these reactions were studied under two different dose rates. The results of this investigation would be elements in the design of a commercial radiation polymerization process which is presently a project of this group.

CHAPTER 2

PROBLEM BACKGROUND

2.1 History of Radiation Polymerization

Although research into the effect of radiation on materials has been in progress for many years, interest in the subject has been greatly stimulated recently by a number of factors, both technical and scientific.

In the development of power from nuclear energy there is a constant search for radiation-resistant materials capable of use in the intense radiation field present in reactors and associated plants. In the chemical industry there has arisen the possibility of inducing useful changes in structure by the use of such radiation fields. Exposure to high energy radiation can promote drastic changes in the physical and chemical properties of solids and this in a quantitative manner which can be readily studied.

The rapid growth of scientific interest in radiation effects can be readily traced in the increasing number of papers, scientific and technical, published on the subject, in the formation of radiation research societies and in the appearance of specialist scientific journals. Industrial applications have also emerged and this is in a relatively few years after the initial fundamental discoveries were made.

One often finds that the most rapid advances occur when two apparently diverse branches of science first converge, and this is

CHAPTER 2

PROBLEM BACKGROUND

2.1 History of Radiation Polymerization

Although research into the effect of radiation on materials has been in progress for many years, interest in the subject has been greatly stimulated recently by a number of factors, both technical and scientific.

In the development of power from nuclear energy there is a constant search for radiation-resistant materials capable of use in the intense radiation field present in reactors and associated plants. In the chemical industry there has arisen the possibility of inducing useful changes in structure by the use of such radiation fields. Exposure to high energy radiation can promote drastic changes in the physical and chemical properties of solids and this in a quantitative manner which can be readily studied.

The rapid growth of scientific interest in radiation effects can be readily traced in the increasing number of papers, scientific and technical, published on the subject, in the formation of radiation research societies and in the appearance of specialist scientific journals. Industrial applications have also emerged and this is in a relatively few years after the initial fundamental discoveries were made.

One often finds that the most rapid advances occur when two apparently diverse branches of science first converge, and this is certainly true in the case of irradiated polymers. Polymer science has only recently become recognized as a distinct branch of science with its own methods, opinions and outlook. Although a few scattered studies describe the utilizing radiation in polymer chemistry before World War II, the extensive development of radiation chemistry of polymeric systems took place during the last three decades, after it appeared that some of the reactions discovered in this field could lead to commercial applications in the near future. These findings have stimulated numerous studies in many laboratories all over the world. Known present commercial radiation processes which are reported in literature are (17):

1) Cross linking of polyethylene films
2) Preparation of special copolymers for battery operators
3) Synthesis of new graft copolymer fibers with improved crease-resistance and soil-release properties
4) Production of wood plastic combinations with improved surface properties and high esthetic appeal.
5) Synthesis of ethyl bromide
6) Controlled degradation of polyox, a polyethylene oxide polymer.

7) Curing of surface coatings by irradiation of specially formulated monomer-based lacquers and paints.

The annual growth rate in recent years for radiation processing of chemicals and plastics has been 20 to 25%.

CHAPTER 3

RADIATION CHEMISTRY

3.1 Various Types of Radiation

The terms 'Ionizing Radiation' or 'High Energy Radiation' usually cover a large number of different types of radiation, some of which are beams of charged particles which directly ionize the molecules of the irradiated medium. The same term also is used to designate other types of radiation such as photons or fast moving uncharged particles.

The second group of radiation comprises electromagnetic waves of high energy, gamma rays and neutrons. According to their definition 'Ionizing Radiations' are capable of producing ions either directly or indirectly in a medium composed of common elements such as air, or water. This implies that the energy of the radiation is higher than the ionization potential of N_2, O_2 or H_2O (i.e., 10 to 15 e.V.). This defines the lower limit of the energy range covered by high-energy radiations. The effective upper limit depends upon the type of radiation and its source. Among all the radio-active isotopes, cobalt 60 is by far the most widely used as gamma ray source in radiation-chemical studies (25, 66).

The practical importance of this isotope has arisen partly because of the ease of its preparation and its fairly long half-life (5.3 years), and partly because of the beam of gamma rays emitted is similar in penetrating power to the radiation emitted by radium (26,66). A good deal of information about different types of radiation is given in (28, 33, 64, 66).

3.2 Interaction of Radiation with Matter

When electromagnetic radiation traverses matter, the absorbed photons are rapidly converted into the fast moving electrons. These electrons produce most of the observed ionizations and are responsible for nearly all the chemical changes that have taken place.

The absorption of electromagnetic radiation in matter follows the familiar expression

$$I = I_0 e^{-\mu x} .$$

Here I is the intensity of the beam, I_0 the original intensity, x the thickness of the absorbing material and μ the total linear absorption coefficient (66).

The various initial chemical species resulting from the interaction of radiation with matter depend to a large extent on the type of radiation used, and this has an important bearing on the subsequent chemical reactions. These various problems are briefly discussed in the following:

(a) Ionization

When a fast electron or any charged particle passes close to a molecule of the absorbing medium, the coulumbic field of the particle strongly polarizes the molecular electrons in their orbitals. If the energy released in this interaction is larger than the binding energy of an electron in its parent molecule, such an electron will be expelled from its orbital and a positive ion is left behind:

$$AB \rightsquigarrow AB^{+} + e \qquad (1)$$

If the positive ion AB^{+} carries an excess of energy, reaction (1) may be followed by a dissociation reaction such as:

$$AB^{+} \rightsquigarrow A^{+} + B \qquad (2)$$

Here B and A are either free radical fragments or stable molecules. The evidence for these processes can be observed in electric discharge reactions of gases (20).

(b) Excitation

If the energy transferred to a molecular electron is lower than its lowest ionization potential, it may still be large enough to displace the electron from its ground state to an 'excited state'. These excited molecules created through direct radiation-chemical interaction such as

$$AB \rightsquigarrow AB^{*}$$

are similar to the corresponding excited state produced through absorption in the same medium of a quantum of light,

$$AB + h\nu \rightarrow AB^{*}$$

and it can be assumed that the subsequent reactivity of such excited molecules is the same, whether the excitation is brought about by a photochemical or radiation chemical act.

(c) Neutron Impacts

Since neutrons do not carry any electric charge, they do not interact with the electronic atmosphere of the molecules in the irradiated medium and their energy is dissipated through direct collision with atomic nuclei. As a result, neutrons are capable of ejecting atoms from their parent molecule, leaving behind a free radical

$$RA \xrightarrow{\text{Neutron}} R^{\circ} + A^{\circ}$$

Here R° is a free radical, and A° a free atom may be in an ionized state.

If the irradiated substance is a crystalline solid, bombardment with fast neutrons produces displacements of atoms from the lattice to interstitial positions, thereby creating lattice defects. These effects can be ignored when dealing with liquids or amorphous solids.

3.3 Ionic and Free Radical Reactions

There are few basic reactions involving active species produced in the primary act. The two most important of these reactions are ionic reaction and free radical reaction.

(a) Ionic Reaction

In a system under steady irradiation, positive ions are generated continuously through primary ionization processes. However, since charges are necessarily created in pairs of opposite signs, an equivalent number of negative charges (i.e., free electrons and negative ions) builds up in the system and charge neutralization occurs by recombination between positively and negatively charged species. Accordingly, two different neutralization processes have to be considered: ion-electron recombination and positive ion-negative ion recombination. In addition ions are capable of initiating chemical changes by reacting with neutral molecules. Finally charge transfer processes may occur between ions and neutral molecules and this reaction may lead to specific changes in mixtures of two or more components. Chapiro has given detailed information on these reactions in (20).

One of the most important of these reactions is the ion-molecular reaction. Chemical reactions initiated by ions are well known in classical organic chemistry, and ionic polymerizations are familiar to polymer chemists. The contribution of ionic reactions in radiation-chemical processes cannot be answered very clearly at present (20). In the early days of radiation chemistry, ions were considered to be responsible for most chemical changes since the production of ions was the most obvious property of ionizing radiations, and the reaction yields were based on ionic yields. In contrast, the modern development of radiation chemistry was until recently, based on the concept that free radicals are the important species which initiate most, if not all, observed reactions. The reason for the lack of reactivity of the ions initially created was accounted for by the fact that such ions only have a very short lifetime in liquids and are rapidly neutralized.

(b) Free Radical Reactions

The importance of excited states and free radicals in radiation chemistry was first emphasized in 1936 by Eyring, Hirschfelder and Taylor (36), and this view has since gained considerable favour among radiation chemists. The departure from the normal behaviour of free radicals which are observed in certain systems were usually interpreted either by assuming that excited molecules or radicals were involved or in terms of radical reactions occuring within the tracks of the ionizing particles. Chapiro has indicated that the predominant radiation chemical changes in many chemical systems are still believed to be caused by free radicals. The following observations can be taken as proof of this idea:

1) radiolysis products of organic substances are similar to the products arising from photolysis of the same compound.
2) several classical free radical chain reactions (polymerization of vinyl monomers, chlorination of hydrocarbons, decomposition of hydrogen peroxide) have been initiated by ionizing radiation and the kinetics show a great similarity to the corresponding reactions initiated by ultraviolet light or chemical initiators (peroxides).

3) conventional inhibitors for free radical reactions are also effective in many cases where the reaction is initiated by ionizing radiation.

Some of the most important elementary free radical reactions are briefly discussed in this section.

(a) Transfer Reaction

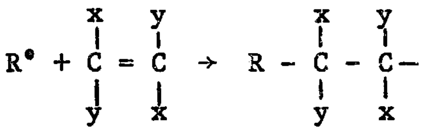
This type of reaction can be written as follows

$$R_1^\bullet + R_2x \rightarrow R_1x + R_2^\bullet$$

where x is an atom such as H, Cl, Br, Na, etc. $R_1^\bullet$ and $R_2^\bullet$ are either free radicals or atoms. For normal hydrocarbon radicals the activation energy for transfer reactions involving H atoms is of the order of 8-12 K cal/mole, which is nearly equal to the chain transfer activation energy in vinyl polymerization

(b) Addition to Unsaturated Molecules

This reaction is the same as propagation step in polymerization processes



$$R^\bullet + \begin{array}{c}x\\|\\C\\|\\y\end{array} = \begin{array}{c}y\\|\\C\\|\\x\end{array} \rightarrow R - \begin{array}{c}x\\|\\C\\|\\y\end{array} - \begin{array}{c}y\\|\\C\\|\\x\end{array} -$$

It requires an activation energy ranging from 4-7 K cal/mole. However, as a general rule, the addition of a free radical on to a double bond requires a lower activation energy than exchange (transfer) reactions.

(c) Destruction Reaction

A free radical can only be destroyed in a given system by interaction with another radical. The corresponding reaction in polymerization is the termination step. Such radical-radical interaction can lead to two distinct processes namely:

i) Combination:

$$R_1^{\bullet} + R_2^{\circ} \rightarrow R_1R_2$$

in which both radicals share their unpaired electrons to form a chemical bond.

ii) Disproportionation:

$$R_1^{\bullet} + R_2^{\circ}\ CH_2 - CH_2^{\bullet} \rightarrow R_1H + R_2 - CH = CH_2$$

Here a hydrogen atom is transferred from one radical to another leaving a double bond.

Combination merely involves the coupling of the two unpaired electrons, and hence does not usually require any activation energy. The termination step in the vinyl polymerization by combination of two growing chains (polymer) usually requires an activation energy less than 2 K cal/mole. Disproportionation on the other hand, usually involves slightly higher activation energies, consequently this reaction is more likely to take place at higher temperatures (20).

It should be noted that free radicals also lose their activity if they are embedded in a viscous or a solid medium. However, the free valency remains unaltered and as soon as the physical state of the medium is changed (for example by an increase in temperature), the radical is again free to react. "Frozen" radicals are formed in radiolysis of polymers and other solid material.

3.4 Radiation Units and Chemical Yields

3.4.1 Radiation Units

The term "Dose" is used to describe in a quantitative manner the radiation received by a given substance placed in the radiation field. This concept of dose implies that energy is transferred from the radiation to the irradiated substance and dose is therefore expressed in ergs per gram of irradiated material.

Absorbed dose of any ionizing radiation is the amount of energy imparted to matter at the place of interest. It is expressed in 'Rads'. The 'Rad' is the unit of absorbed dose and is 100 ergs per gram or 6.25×10^{13} electron volts per gram.

(a) Intensity of Radiation and Radioactive Source

Radioisotopes emit high energy radiation by a rearrangement of an unstable nucleus. The intensities of such sources of radiation are expressed in 'curies'.

The 'curie' is the amount of a radioactive element in which there are 3.7×10^{10} disintegrations per second. Thus a source of

C curies emitting gamma radiation of E M.e.V. will emit:

$$3.7\text{x}10^{10}\text{x}10^{6} \text{ E x C x e.V./sec. or } 5.92\text{x}10^{4} \text{ E x C ergs/sec.}$$

In many cases the disintegration of a radioactive nucleus gives rise to other unstable nuclei which disintegrate in their turn and contribute to the energy emitted. To obtain the total energy produced by such isotopes, it is therefore necessary to add together the energy of each of those successive radiations. For Co^{60} two gamma photons of energies 1.33 and 1.17 M.e.V. are emitted. The energy output per curie of cobalt 60 is therefore 5.92 x (1.33 + 1.17) = 14.8 milliwatts/curie.

The intensity of radiation is defined as the energy flowing through unit area perpendicular to the beam per unit time and expressed in ergs per square centimeter - second.

There are some other radiation units such as roentgen, Rep, pile unit, absorbed dose rate etc., which have been defined completely in (29, 34, 66).

3.4.2 Radiation-Chemical Yields

The yields of radiation-induced reactions were originally expressed in terms of the ionic yield M/N, defined as the number of the molecules of a specified type changed per ion pair formed in the medium. However, ionization cannot be measured accurately except in the gas phase and consequently the term 'G Value' has been introduced.

G Value

The chemical changes which occur for a given amount of absorbed energy are now almost accepted as the method for expressing yields.

Burton (35) has introduced the 'G' symbol for expressing radiation chemical yields and defined 'G Value' for a given irradiated system as the absolute chemical yield expressed as the number of individual chemical events occurring per 100 e.V. of absorbed energy.

When the system of interest involves a chain reaction, G Values for G(M) or G(Products) may become extremely large, of the order of 10^5 or 10^6 or even more (20) and in addition the yields strongly depend on physical factors such as temperature, dose rate, viscosity of the medium, etc., which can influence any of the elementary reaction steps involved (25). Low G Values signify radiation resistance.

CHAPTER 4

RADIATION INITIATED POLYMERIZATION

4.1 Introduction

There are probably few polymers or monomers which have not been subjected to high energy radiation in a planned or even speculative manner during the past 15 years.

The radiation-initiated polymerization of vinyl monomers is a direct application of radiation chemistry to the synthesis of high polymers. It is now well established that the initiation step in addition polymerization requires the admittance of some external energy. In radiation polymerization this energy is supplied by the ionizing radiation. However, once the reaction chains are started they proceed to grow according to conventional kinetics rules.

The use of ionizing radiation as a 'catalyst' for initiating the chain polymerization of vinyl monomer is not a new application since experiments along these lines were reported in 1938 (40).

The important fact is, however, that radiation has been demonstrated to be a competitive initiator system for polymerization reactions. Chapiro has gathered a good deal of information on the developments in this field covering the period up to 1962.

Huglin (25) and Ballantine (17) have published more recent reviews on radiation as a polymerization tool and process radiation development respectively.

4.2 Mechanism of Radiation Polymerization

4.2.1 Ionic Mechanism

The mechanism of production of positive and negative ions through primary ionization processes is discussed in Section 3.3. More recently experimental evidence has been obtained which shows that ionic chain polymerizations can also be initiated by radiations.

In order to understand why ionic polymerizations are not usually initiated by the primary ions at room temperature, it is important to take into account the fact that the ions formed in irradiated liquids are believed to have a very short life time, in the order of 10^{-13} seconds. It should be noticed furthermore, that rather critical experimental conditions are required for ionic polymerization to take place. On the other hand, ionic polymerization mostly occur at very low temperatures. Shimomura et al (37) have shown that the anionic polymerization of styrene in tetrahydrofuran has negative apparent activation energy around 0°C. The low temperature polymerization of styrene dissolved in various chlorinated solvents provides another example of radiation-initiated polymerization occurring by a cationic mechanism.

The contribution of the ionic mechanism was found to increase with dose rate as expected from the kinetics of these processes. Chapiro (23, 55) has considered a first order reaction for the rate of ionic polymerization of styrene with respect to dose rate (i.e., $R_p \propto I^n$ which $n = 1$). Katsujiueno et al (9) has studied the radiation induced ionic polymerization of bulk styrene under extremely dry conditions. They have found that the rate R_p of polymerization increases with more rigorous drying of the monomer and this effect is accompanied by a change in the exponent n for the dose rate (I) dependence of R_p, from n values near unity to 0.6. A mechanism involving trimolecular termination of free ions is thereby indicated.

The various results are consistent with the assumption that a cationic mechanism is responsible for the radiation-initiated polymerization of styrene under these experimental conditions. The cationic reaction is favoured in the presence of solvents having a high dielectric constant, and since it exhibits a negative activation energy, it is particularly marked at low temperatures.

At higher temperatures the free radical process is usually much more pronounced, however, a significant contribution of the ionic mechanism is also found at room temperature (71). It should be noted that since the order of the ionic process with respect to the radiation dose rate is nearly 1, while that of the free radical reaction is $\frac{1}{2}$, one can expect that the importance of the ionic contribution to the reaction will depend strongly upon dose rate. Thus the ionic contribution should be negligible at very low dose rates whereas if radiations of very high dose rate are used, such as for the electron beams produced by accelerators, the polymerization of styrene should occur almost exclusively by the ionic mechanism, even at room temperature. This last conclusion is further supported by the fact that long chain free radical polymerization cannot occur at very high dose rates owing to the recombinations involving primary radicals (4). It should be pointed out that the rate of most of the ionic reactions are unaffected by the presence of oxygen or other free radical scavengers.

4.2.2 Free Radical Mechanism

The radiation-initiated polymerization of vinyl monomers leads to high molecular-weight products having properties almost identical to those of the corresponding polymers obtained when using conventional methods of initiation. It can thus be concluded that radiation polymerization proceed by a long-chain reaction process similar to ordinary polymerization.

From the considerable amount of experimental data now available, it becomes apparent that in most cases radiation polymerization can be fully accounted for by free radical processes. Some evidence of free radical mechanisms are as follows:

1) action of free radical inhibitors:

   The earliest experiments in the field of radiation polymerization showed that compounds which are known to inhibit free radical reactions, also inhibit radiation-initiated polymerizations.

2) studies in copolymerization:

   The chemical composition of a compolymer A_pB_q is a function of the relative reactivities of the two monomers with respect to the active end groups of the growing chains (55). It has been shown that an equimolar mixture of styrene and methyl-methacrylate when polymerized by free radical initiators led to a copolymer containing 50% styrene, 50% methyl-methacrylate, with anionic initiators the resulting polymer is essentially pure methyl-methacrylate. In all cases the copolymer obtained by irradiating an equimolar mixture of styrene and methyl-methacrylate at room temperature contained approximately 50% of each of the two components (55).

3) Temperature coefficients:

Ballantine et al have shown the overall activation energies for styrene and methyl-methacrylate polymerized by gamma-rays are 7.15 and 4.9 K cal/mole respectively. Positive activation energies were also observed by some other workers (55) in gamma-ray initiated polymerization of styrene. The absolute values of these activation energies were of the expected order of magnitude for free radical polymerization in which the initiation step is temperature independent. In contrast ionic polymerizations usually exhibit either very low or even negative overall activation energies (37).

4) Kinetic analysis:

The rate of polymerization of numerous monomers is found to be proportional to the square root of the radiation dose rate at low temperatures. Such a behaviour conforms to free radical initiation. From the data presented above, the general conclusion can be derived that radiation polymerizations of most vinyl monomers proceed via free radical mechanisms above room temperature.

4.3 Kinetics of Radiation-Initiated Free Radical Polymerization

The study of the radiation-initiated polymerization of those vinyl monomers which polymerize in homogeneous media is of particular interest since these reactions have been investigated with conventional means of initiation and full quantitative treatments are available for the kinetics of a number of specific systems. The radiation initiated polymerization of styrene was extensively investigated by numerous workers who used gamma-rays.

It is now generally accepted that the free radical addition polymerization proceed via a classical chain reaction involving the three major elementary steps of initiation, propagation and termination (31).

In radiation polymerization absorption of radiation energy finally leads to the production of free radicals. The free radicals adds on to a double bond of a monomer molecule in propagation steps and generate another free radical.This process goes on until the activity of the growing polymer chain is destroyed. This process is known as termination.

In homogeneous liquid phase polymerization, chain termination occurs almost exclusively by mutual interaction of two radicals, leading either to combination with the formation of a single polymer molecule or to disproportionation by the transfer of a hydrogen atom from one radical to the other, the latter process giving rise to one saturated and one unsaturated molecule. The steps can be shown as follows:

INITIATION $A \rightsquigarrow 2R^{\bullet}$ RATE = R_i

If only pure monomer is subjected to the radiation, initiation step is limited to:

$$M \rightsquigarrow 2R^{\bullet}$$

and the rate of this reaction is:

$$R_i = \phi_M I[M]$$

where $\phi_M[M]$ is the rate of production of free radicals in the monomer, expressed in moles per liter per unit radiation dose, and I is the dose rate.

PROPAGATION RATE

$$R^{\bullet} + M \longrightarrow RM^{\bullet}$$

$$RM^{\bullet} + M \longrightarrow RM^{\bullet}_{n+1} \qquad K_p[RM^{\bullet}][M]$$

TERMINATION RATE

By Combination

$$RM_n^\bullet + RM_m^\bullet \rightarrow P_{m+n}$$

By Disproportionation

$$RM_n^\bullet + RM_m^\bullet \rightarrow P_n + P_m \qquad K_t[RM^\bullet]^2$$

A, is any molecule in the reacting mixture, $R^\bullet$ radical, M is the monomer, $RM_n^\bullet$ growing chain, and P_n is the dead polymer. Another elementary step of importance is the chain transfer

$$RM_n^\bullet + SX \rightarrow RM_nX + S^\bullet \qquad K_{tr}[RM^\bullet][SX]$$

SX is either the monomer or any added substance such as a solvent. Since a growing chain is stopped in the process, chain transfer necessarily lowers the average molecular weight (31). This happens when $S^\bullet$ is a reactive radical. If it is not then it is called degradative chain transfer.

Assuming a stationary state, then

$$R_i = K_t[RM^\bullet]^2$$

If the kinetic chain is long, the overall rate is

$$R = K_p[RM^\bullet][M] = K_pK_t^{-1/2}R_i^{1/2}[M] \qquad (1)$$

This was a classical kinetic equation for polymerization where R is proportional to the square root of the R_i.

In the case of pure monomer subjected to ionizing radiation, the overall rate of polymerization is equal to

$$R = K_p K_t^{-1/2} \phi_M^{1/2} I^{1/2} [M]^{3/2}$$

or

$$R = K_p K_t^{-1/2} (\phi_M I)^{1/2} [M]^{3/2}$$

If the rate of initiation increased by the use of higher dose rates, the simplified kinetic scheme no longer applied to the system. In this case the following detailed kinetic scheme which is proposed by Chapiro is applicable.

A. INITIATION	RATES
$A \rightsquigarrow 2R^{\bullet}$	$R_i = \phi_A I[A]$
B. RECOMBINATION OF FREE RADICALS	
$R^{\bullet} + R^{\bullet} \rightarrow R_2$	$K_{oo}[R^{\bullet}]^2$
C. ADDITION TO MONOMER	
$R^{\bullet} + M \rightarrow RM^{\bullet}$	$K_{po}[R^{\bullet}][M]$
D. PROPAGATION	
$RM_n^{\bullet} + M \rightarrow RM_{n+1}^{\bullet}$	$K_p[RM^{\bullet}][M]$
E. MUTUAL TERMINATION	
$RM_n^{\bullet} + RM_m^{\bullet} \rightarrow P_{m+n}$ or $(P_m + P_n)$	$K_t[RM^{\bullet}]^2$

F. TERMINATION BY PRIMARY RADICALS

RATES

$$RM^{\bullet} + R^{\bullet} \rightarrow P_n \qquad K_{to}[RM^{\circ}][R^{\circ}]$$

K_{oo}, K_{to} and K_t all pertain to mutual interaction of two free radicals. Such reactions proceed very rapidly and only require a low energy of activation, if any. The absolute values of these rate constants are usually of the order of 10^6 or 10^9 liter $mole^{-1}$ sec^{-1}. The order of these rate constants are

$$K_{oo} > K_{to} > K_t$$

The second group of rate constants comprises K_{po} and K_p which both correspond to addition reactions of a free radical to vinyl double bond. The required energy of activation is about 5 to 8 K cal/mole and the absolute values of these rate constants at room temperature are of the order of 10 to 10^3 liter/mole sec. (55).

Assuming stationary state then

$$\frac{d[R^{\circ}]}{dt} = 0$$

$$[R^{\circ}] = \frac{K_{po}[M]+K_{to}[RM^{\circ}]}{2K_{oo}} [\{1+ \frac{4K_{oo}\ R_i}{(K_{po}[M]+K_{to}[R^{\circ}M]^2)}\}^{\frac{1}{2}} - 1] \qquad (2)$$

$$[RM^{\bullet}] = \frac{K_{to}[R^{\bullet}]}{2K_t} [(1 + \frac{4K_{po}K_t[M]}{K_{to}^2[R^{\bullet}]})^{\frac{1}{2}} - 1] \qquad (3)$$

The overall reaction rate

$$R = K_p[RM^\bullet][M]$$

cannot be expressed explicitly in terms of known reagent concentrations. Equations (1) and (2) can be simplified for various limiting cases which arise according to the magnitude of the dose rate. For very low dose rates, concentration of $R^\bullet$ and $RM^\bullet$ are very low so the overall reaction rate can be written

$$R = K_p\ K_t^{-1/2}\ R_i^{1/2}[M] \tag{4}$$

This result shows that all primary radicals are trapped by the monomer or reaction (B) and (F) do not occur to appreciable extents. At higher dose rate the rate of reaction can be written as follows

$$R = \frac{K_{po}}{(2K_{oo})^{1/2}} \cdot \frac{K_p}{K_t^{1/2}} [M]^2 \left[\left(1 + \frac{4K_{oo}R_i}{K_{po}{}^2[M]^2}\right)^{1/2} - 1\right]^{1/2} \tag{5}$$

This equation shows that if the dose rate reaches such a magnitude that

$$R_i << (K_{po}{}^2[M]^2/4K_{oo})$$

fails to apply, the classical dependence of reaction rate on the square root of rate of initiation no longer holds and the overall rate rises more slowly than $R_i^{1/2}$.

The last limiting case which can be considered is in a very high dose rate, one can assume

$$R_i >> K_{po}^2 [M]^2/4K_{oo}$$

Then
$$[R^\bullet] = R_i^{1/2}/K_{oo}^{1/2}$$

and
$$[RM^\bullet] = K_{po}[M]/K_{to}$$

The overall rate of reaction becomes

$$R = K_pK_{po}[M]^2/K_{to} \tag{6}$$

This equation shows that for very high rates of initiation, the polymerization rate reaches a limiting value which does not increase further when the rate of initiation rises (55). This situation corresponds to a system in which all growing chains are terminated by primary radicals, i.e., in which reaction (E) does not occur to appreciable extent. It should be noted that this last limitation only arises if the stationary concentration of radicals R$^\bullet$ is very large. It follows that the molecular weight of the polymer formed in such a system is necessarily low. If the average degree of polymerization only corresponds to a small number of monomer units, one can no longer assume that the overall reaction rate is equal to the rate of chain propagation, since the rate of monomer consumption through step (C) may then become appreciable. The overall rate of monomer consumption is given by (55):

$$R = K_{po}[R^\circ][M] + K_p[RM^\circ][M]$$

or

$$R = K_{po}[M]^2 \left(\frac{K_p}{K_{to}} + \frac{R_i^{1/2}}{K_{oo}^{1/2}[M]}\right) \tag{7}$$

But if the rate of initiation increases to such an extent that

$$R_i^{1/2} >> K_p K_{oo}^{1/2}[M]/K_{to}$$

then

$$R = K_{po} K_{oo}^{-1/2} R_i^{1/2} [M] \tag{8}$$

Equation (8) is formally the same as the classical equation (1), but here the rate constants K_{po} and K_{oo} appear instead of K_p and K_t respectively. Hence it can be concluded that when the above situation arises any chain that is initiated by step (C) is immediately terminated by step (F) and no true chain propagation can occur. The reaction product obtained in this situation have a very low molecular weight.

4.3.1 Influence of Dose-Rate

The radiation-initiated polymerization of styrene has been studied over an extremely broad range of dose rate. Almost all of the published results (16) have led to the classical square-root relationship between the reaction rate and activity of the source at temperatures below 75°C. Manowitz et al (40) who worked with Cobalt 60 and Tantalum 182, gamma-rays reported a first order relationship between the rate of polymerization and dose rate in the range of 38 to 90 Rads/sec. The experimental rates reported by this group of investigators were much lower than the values reported by other workers on the basis of square-root law.

The results showed that the square-root relationship held down to the lowest dose rate investigated, but at higher dose rates, the exponents decreased to slightly less than 1/2 (4, 41). The degree of polymerization of the polymer showed similar deviations from the inverse-square-root relationship. The result was interpreted by assuming that the monomer could not react with all the primary radicals formed at the higher dose rates and that some of these free radicals recombined without initiating polymerization (4).

The data obtained by Sood (16) and Srinivasan (43) at temperatures below 75°C confirms the square-root relationship. However, above 74°C, the values of (n) decreases linearly with rising temperature, until above about 109°C the rate of conversion becomes independent of dose rate. A similar trend of the temperature dependence is also reported by these authors for the average degree of polymerization $\bar{P}_n$. This dose rate independence is ascribed to a "limiting rate of initiation", characteristic of the intensity range. They have predicted that this phenomenon can be expected in any vinyl monomer where the monomer is fairly active, and produces relatively stable radicals. For further information the reader is referred to reference (16).

4.3.2 Influence of Reaction Temperature

In order to normalize the various results it has been implicitly assumed that the initiation step in radiation polymerization does not require any energy of activation and that the activation energies of propagation and termination are identical with those determined with conventional means of initiation. This assumption seems justified in view of the similarities found for general kinetic features of the polymerization of styrene when initiated either by radiation or by conventional means. Cohen (42) has mentioned that with a change in temperature of reaction the rates of all different stages of polymerization will change and it is not clear which of these steps is most important in leading to the observed effects of temperature change on polymerization reactions. As the temperature is raised in thermal polymerizations the rate increases and the molecular weight or degree of polymerization of the product decreases.

However, in radiation induced polymerization of styrene the temperature dependence may be more complicated at high dose rates, when the various reactions involving primary free radicals effectively compete. In such an event, an increase in the temperature is expected to favour the addition of free radicals to the monomer with respect to radical-radical interactions and accordingly the overall reaction rate is expected to rise more rapidly with temperature than at lower dose rates.

Chapiro has considered the three reaction steps involving primary radicals $R^\bullet$ as follows:

$$\text{(B)} \quad R^\bullet + R^\bullet \rightarrow R_2$$

$$\text{(C)} \quad R^\bullet + M \rightarrow RM^\bullet$$

$$\text{(F)} \quad R^\bullet + R^\bullet M_n \rightarrow P_n$$

The general features of the overall process are determined to a large extent by the results of the competition of these three reactions. If reaction step (C) dominates, all primary radicals will be used to initiate polymerization. It can be seen that since the rate of reaction (C) is

$$R(C) = K_{po}[R^\bullet][M]$$

this reaction is slowed down independently of (B) and (F) if either K_{po} is very small or [M] is low. K_{po} is the rate constant of the elementary reaction and is closely related to the propagation step in vinyl polymerization, so step (C) should require an energy of activation of the order of 5 to 8 K cal/mole and that its magnitude will depend on the reactivities of both the radical $R^\bullet$ and the double bond of monomer M.

The other two reaction steps (F) and (B) involve free radical combination (or disproportionation) reactions. They only require a very low activation energy and are not related whatsoever to the reactivity of the double bond of the monomer. So

i) For a given monomer system, an increase in temperature should chiefly favour reaction (C) in its competition with (E) and (F).

ii) For a given reaction temperature, reaction (C) will be favoured if a highly reactive monomer is used.

On the other hand, in simplified kinetic schemes the overall activation energy of the reaction can be easily calculated

$$E = \frac{1}{2} E_i + E_p - \frac{1}{2} E_t$$

Here E is the overall activation energy, E_i, E_p and E_t are partial activation energies for initiation, propagation and termination respectively.

E_p is approximately 5-8 K cal/mole for most monomers, E_t ranges from 0 to 2-3 K cal/mole. The magnitude of E_i depends upon the type of initiation involved. For thermal or chemical means of initiation, E_i is usually of the order of 25 to 30 K cal/mole, while for photochemical or radiation-chemical initiation $E_i = 0.0$. So, the overall activation energies are as follows:

$$E_{\text{Thermal}} = 14 + 7 - 1 \cong 20 \text{ K cal/mole}$$

$$E_{\text{RAD.}} = 0 + 7 - 1 = 6 \text{ K cal/ mole}$$

The results clearly show that the rates of radiation polymerization and photo-polymerization rise much more slowly with temperature than the rate of the thermal initiated reaction. When applying the same reasoning to the molecular weight, it immediately appears that in thermal temperature, whereas in radiation polymerizations the molecular weight rises in the same ratio as the overall rate, provided however, that chain transfer is negligible. If this last condition is not fulfilled, the molecular weight of radiation polymer may either rise or drop with temperature or even show a maximum at a given temperature depending on the relative importance of transfer and propagation (55).

As a general rule, however, one can expect that an increase in temperature will increase the mobility of, and the accessibility to the growing chains, and if termination is the controlling step the overall rate is expected to decrease. If however, propagation is the controlling step an increase in temperature should lead to a very fast increase in the overall rate (55).

4.3.3 Degree of Polymerization

Assuming the number-average degree of polymerization $\bar{P}_n$ is identical to kinetic chain length, i.e., that chain transfer reaction can be neglected, the following expressions are obtained for $\bar{P}_n$ in the various situations.

1) If the kinetic chain length is equal to the amount of polymer produced divided by the total number of polymer chains started, this ratio is equal to the ratio of the overall reaction rate to the rate of chain initiation.

Assuming that termination occurs exclusively by disproportionation

$$\bar{P}_n = R/R_i = K_p K_t^{-1/2} \; R_i^{-1/2}[M] \tag{9}$$

or if termination occurs by combination of two growing chains

$$\bar{P}_n = 2 \; K_p K_t^{-1/2} \; R_i^{-1/2}[M] \tag{10}$$

If transfer by the monomer or solvent becomes operative

$$1/\bar{P}_n = \frac{K_t^{1/2}}{K_p} \cdot \frac{R_i^{1/2}}{[M]} + \frac{K_{trm}}{K_p} + \frac{K_{trs}}{K_p} \frac{[S]}{[M]} \tag{11}$$

The above situation will be encountered for very low dose rate.

2) At higher dose rates the degree of polymerization in the case of termination by disproportionation is given by

$$\bar{P}_n = R/K_{po}[R^\bullet][M] \quad .$$

hence

$$\bar{P}_n = \frac{(2K_{oo})^{1/2}}{K_{po}} \cdot \frac{K_p}{K_t^{1/2}} \left[\left(1 + \frac{4K_{oo}\, R_i}{K_{po}^{\,2}[M]^2}\right)^{1/2} - 1\right]^{-1/2} \qquad (12)$$

If termination occurs by combination $\bar{P}_n$ is twice as great.

3) At very high dose rate where termination occurs exclusively by reactions involving primary radicals $R^\bullet$ (reaction F)

$$\bar{P}_n = R/K_{po}[R^\bullet][M]$$

hence

$$\bar{P}_n = K_p(K_{oo}^{\;1/2}/K_{to})\; R_i^{\;-1/2}[M] \qquad (13)$$

This equation shows that when this situation arises although the overall rate becomes independent of the rate of initiation (55) the degree of polymerization of the resulting polymer still decreases proportionately to the square root of the rate of initiation (55).

As is clear from Equation (9), the molecular weight of the radiation polymer is expected to increase with rising temperature. The increase of molecular weight with temperature is clearly apparent from Table V.II (4). It can be seen however that this effect is much less pronounced than the corresponding increase of the reaction rates, a result which is presumably caused at least in part by the increased importance of chain transfer by the monomer as the temperature rises (4). Cohen (42) has mentioned the same point for catalyzed polymerization of styrene. He has concluded that when radicals are generated at equal rates at several temperatures both the rate of polymerization and the molecular weight of the product are greatest at the highest temperature. He has pointed out that there should not be any chain transfer reaction, and numbers of chains started at three temperatures should be equal. Ballantine et al (44) and Srinivasan (43) also have found the same results in radiation initiated polymerization of styrene and methyl-methacrylate. They expressed the view that since the initiation rate is presumably independent of temperature and only the propagation and termination rates are affected, so the molecular weight increase with increasing temperature. Nearly almost all of these data are gathered from experiments conducted at temperatures below 100°C.

4.4 High Conversion Kinetics of Radiation Polymerization of Styrene

Most theoretical approaches and experimental studies on the polymerization of styrene are directed to the region of low conversion, whereas the commercial preparation of polystyrene usually involves carrying the polymerization reaction almost to completion. This gives rise to a number of complex but practical questions, which have not even received adequate experimental attention.

One question about high conversion concerns molecular weight as a function of conversion. Early studies indicated a tendency for the molecular weight to remain constant if the monomer was pure (67). Roche (67) finds that there is usually a maximum in the molecular weight conversion curve for thermal polymerization. The height of the maximum is definitely related to the purity of the monomer. He finds that with peroxide catalyzed polymerization the molecular weight remains constant until the peroxide is consumed and then increases at high conversions. Hui (18) has given a good deal of information and references on this subject in the case of conventional polymerization of styrene.

In the case of radiation polymerization of styrene the polymerization rate curve exhibits three distinct phases, the nature of which are determined by the polymerization conditions.

1) An initial slow period at the beginning of the reaction which according to Ballantine and Srinivasan (43, 44) for styrene at 25°C this section will continue up to 50 to 60% conversion. This phenomenon has been observed by the other workers in the field (14, 16).

2) A period of relatively rapid polymerization which persists almost to the end of the reaction, and for which the rate is exponentially dependent upon temperature. This may be explained on the basis of a 'Trommsdorf' effect in which the termination is diffusion dependent, as viscosity increases the diffusion and termination rate decreases. A good deal of information on this subject has been collected by Boundy and Boyer (67).

3) A final slowing down in rate as the reaction approaches completion and the monomer becomes exhausted. This slowness of the rate of polymerization at conversions above 90% has an important bearing on the nature of the finished product since any monomer remaining in the polymer acts first to plasticize the polymer and reduce its heat distortion temperature, and secondly to produce blushing and crazing with age as the monomer evaporates. In the case of styrene an 'S' shaped curve was reported by a number of workers (16, 44).

The temperature of the reacting medium was measured by several investigators in the course of the reaction and it was noted that the acceleration period is accompanied by considerable overheating of the system. This increase was measured by Ballantine (44) and in the case of styrene was 7°C at room temperature and 14° at 72°C. Such a small increase could not account for the rapid increase in the rate observed. During the methyl-methacrylate polymerizations increases of 40° at -18°C and 100° at 25°C were observed, and in this case the higher temperature undoubtedly contributed to the increased rate.

As it is mentioned by Chapiro (4) this critical conversion depends on both the dose rate and the reaction temperature. There are some complications which will be created by non-isothermal conditions arising in the gel effect, because as it can be seen, the increase in the reaction rate is concomitant with an increase in molecular weight of the polymer. These various facts could indicate that a conventional gel effect is operating in the system. The interpretation of a simultaneous increase of the reaction rate and the molecular weight of the resulting polymer can be based in principle on the assumptions of either an accelerated propagation or a reduced termination rate. The second assumption seems more likely on theoretical grounds and can be readily accounted for when considering that termination by mutual interaction of high molecular weight growing chains becomes diffusion controlled in the highly viscous medium. According to Chapiro (55) once the reaction medium in polymerization reactions at high conversions has reached a critical viscosity, the growing polymer chains are trapped in the gel-like phase and termination by interaction of two active chain ends becomes highly unlikely or even impossible.

For a given monomer this critical viscosity is reached for a degree of conversion which depends upon various physical factors of the reaction. But the controlling factors seem to be the molecular weight of the polymer formed during the first part of the reaction and the temperature. A still different unsolved question arising at high conversion concerns the effect of existing polymer. In the case of radiation the observed acceleration can be attributed partially to an increase in the rate of initiation as the reaction proceeds. Chapiro (4) has predicted a greater sensitivity of polystyrene to radiolysis than of styrene monomer (because of less resonance stabilization of polystyrene), consequently expecting the total rate of initiation to be approximately 1.5 times higher than the rate of initiation in the pure monomer. Dean (14) and Elaraby (15) have shown conclusively that

$$G_{\text{Polymer}} \approx G_{\text{Monomer}}$$

which contradicts Chapiro's prediction. Dean (14) argues that if the concentration of free radicals which will actively result in the consumption of monomer molecules has a maximum limit, then this limit would also apply to free radicals generated in the polymer. It is also mentioned that if the assumption of limiting free radical concentration is true, then increasing the dose rate should not give higher conversions. In other words, increasing the dose rate should not result in an increase of effective G_R, but should decrease it, in order to keep the product of G_R and dose rate relatively constant. Elaraby's data (15) has shown good agreement with the assumption of $G_R^P \approx G_R^M$. In the course of initiation by polymeric radicals the polymer is itself radiolyzed and the polymeric free radicals thus generated and contribute to the chain initiation

$$P \rightsquigarrow 2P^{\bullet} \qquad \text{RATES} = G_R^P\,[P]$$

Here $P^{\bullet}$ is a polymeric radical. 'P' usually has a chemical structure similar to that of 'M' and hence energy transfer processes should be minimized. However, since the monomer molecule contains a double bond, it may be more strongly stabilized by resonance than the corresponding polymer and accordingly G_R^P may be larger than G_R^M. It follows that in such systems the rate of initiation should steadily increase with conversion, and this effect may become very important at high conversions, when most chains initiated by radicals generated from the polymer (55). For polystyrene the G_R^P has been reported by Chapiro (24), to be in between 1.5 and 3. This value is between two and one-half to four and one-half times G_R^M value for the monomer.

The polymer molecule resulting from chain initiation by a polymeric radical will have a much higher molecular weight then if small radical $R^{\bullet}$ are involved. Furthermore, if $P^{\bullet}$ is formed through scission of a side-group of the polymer molecule, the resulting polymer will have a branched structure.

It can be concluded that the simplified classical radiation polymerization kinetics do not apply at high conversions. No attempt was made, however, to develop the complete polymerization kinetics.

4.5 High Temperature Radiation Polymerization of Styrene

Thermal polymerization of styrene was reported as early as 1845 (3). Then many workers studied the thermal polymerization of styrene with various theories being proposed. Gamma radiation polymerization of styrene and some other monomers were conducted by several workers up to 72.0°C (44, 43).

Only recently, the work has been done up to 110°C on styrene (16). Thermal polymerization data before 1952 are compiled by Boundy and Boyer and radiation polymerization dated up to 1962 are collected by Chapiro. Hui (18) has reported some thermal data at temperatures above 150°C. His results indicated the rate of thermal polymerization followed the Arrhenius type relationship with temperature and that the molecular weight of polymer decreases significantly with rise of reaction temperature (18, 42).

There have been, however, few attempts to discuss quantitatively the equilibrium distribution that must exist between polymerized and unpolymerized material as a function of temperature. It has generally been tacitly assumed that in a certain temperature range polymers will keep growing in size, restricted only by the kinetic situation, until all the monomer and short polymers are incorporated into one giant molecule. It is however well known that polymers, such as polystyrene and many other chain polymers will break down at high temperature and give a large percentage of monomeric material (45). It is also known that polymers formed at high temperatures generally have a lower average molecular weight than those formed at low temperatures (18, 45).

It is reported by Stull (22) that at high temperature styrene might be dehydrogenated and give ethylnylbenzene (phenyl acetylene) plus ethylbenzene.

$$2 \text{ Styrene} \rightleftarrows \text{ethynylbenzene} + \text{ethylbenzene.}$$

$\Delta H°$ of this reaction at 227°C is 9.581 K cal/mole, $\Delta F°$ = 11.876 K cal/mole and $K_p = 6.45 \times 10^{-6}$ atmosphere (equilibrium constant) Figure 3-13 of Page 72 (22) shows the equilibrium composition for this reaction as a function of temperature. As one can see the curve indicates that even at room temperature the equilibrium calls for 1 or 2 parts of phenylacetylene per million of styrene and that this amount increases as the temperature is raised. On the other hand, this substance is a good inhibitor for polymerization of styrene as is mentioned in (46). Since its boiling and freezing points are so near to those of styrene, it will not be removed by the usual purification procedures of distillation and crystallization.

The contribution of thermal polymerization in the radiation polymerization of styrene was accounted for by Sood et al (16) assuming the rates of initiation thermally and from irradiation were additive, i.e.,

$$R_{i(total)} = R_{i(\gamma)} + R_{i(TH)}$$

and the rate of polymerization can be calculated from the following equation introduced by Srinivasan (43)

$$R_{Rad} = (R^2_{total} - R^2_b)^{1/2}$$

R_b is the rate of blank reaction or rate of thermal reaction. Calculations indicated that the contribution of thermal polymerization was not significant for temperatures 74°C and below (14, 16).

The rate of initiation for radiation was far greater than the thermal initiation rate. It has been mentioned elsewhere in this report that the rate of radiation polymerization is very sensitive to the presence of impurities (experimental section) as well as atmospheric oxygen (for styrene polymerization). The significance of thermal polymerization in radiation polymerization is believed to be dependent on the relative contribution of rates of initiation, which in turn depends on the monomer and the dose rate under consideration.

4.6 Degradation and Depolymerization

As the double bond disappears to form polymer heat is evolved and this favours polymerization. On the other hand, when the free monomer molecules are linked into long polymer chains the entropy decreases and this tendency favours depolymerization. While long chains can be formed at low temperatures, yet the same polymer will split off monomer units when taken to a much higher temperature.

In spite of the complex sequence of events which occur in irradiated polymers between the initial event (ionization or excitation) and the final crosslinked or degraded product, the overall reactions are surprisingly simple.

It is reported by Charlesby (69) that both the degree of crosslinking and degree of degradation are directly proportional to the radiation dose and are independent of its intensity. Most polymers appear to fall into two distinct classes, those which crosslink and those which degrade.

Polystyrene is considered to be in the first class (i.e., crosslinked). Any theory of the mechanism of crosslinking and degradation must account for phenomena such as the temperature dependence of crosslinking and degradation, and for the reduction in these effects when certain additives are incorporated. In the case of degradation, the lack of an intensity dependence offers no serious difficulty, but for crosslinking where each crosslink involves two polymer molecules, it imposes certain restrictions on the type of reaction. Charlesby (61) has given a good discussion about this subject. For the polymerization of styrene at higher temperature, both forward polymerization and the reverse depolymerization processes have to be considered. The significance of depolymerization will be dependent on temperature (18). For styrene-polystyrene systems, it has been indicated that the rate of depolymerization is not significant below 150°C, but increases with increase in temperature until the ceiling temperature is reached at which the free energy of formation of polymer from the reactants is zero, hence

$$T_X = \Delta H_X/\Delta S_X$$

where ΔH_X and ΔS_X are the increments of T_X of heat content and entropy per mole of monomer polymerized. The ceiling temperature, which presumably marks the reversal of the propagation reaction is calculated at 276°C for gaseous styrene monomer to condensed polymer (67).

Most of the published data on degradation or crosslinking of polystyrene caused by radiation are at low temperatures (47), and there are no available data at temperatures above 150°C where the contribution of thermal initiation in radiation polymerization becomes significant.

CHAPTER 5

EXPERIMENTAL

For details of sample preparation and analysis see Appendix A.

5.1 Reagents and Analytical Techniques

Uninhibited styrene which was provided by Polymer Corporation Ltd., Sarnia, Ontario, was used. This styrene monomer was used for all polymerization reactions without further purification, since the applicability of this work to industrial practice was considered of importance.

The monomer analysis which was provided by Polymer Corporation is given in Table 5.1.1.

All the solvents used in the courses of different analyses were purchased and were again used directly without further purification. A list of these solvents is given in Table 5.1.2.

5.2 Reactor

All polymerization reactions were carried out in double sealed pyrex glass vials. Four sizes of vials (5 MM, 7 MM, 8 MM and 18 MM O.D.) were tested and finally the 7 MM O.D. size was chosen as the most satisfactory.

The vials were held in circular slots which were welded to the outer cylinder of the source holder illustrated in Figures A.1.3.1 and A.1.3.2 of Appendix A. The source consisted of 12 pencils of Co^{60} and has been fully described in (48) and Figure A.1.1.1. The entire assembly was enclosed in an oil bath, with the sample in direct contact

TABLE 5.1.1

Analysis of Styrene Monomer

COMPONENTS	WEIGHT %
Styrene	99.630
Ethyl Benzene	0.032
Isopropyl Benzene	0.123
N-Propyl Benzene	0.090
Sec-Buthyl Benzene	0.039
α-Methyl Styrene	0.037
Sulphur	0.0004
Chlorides	0.0001
Benzaldehyde	0.0012
Polymer	0.0016
Water	Saturated (500 ppm)

TABLE 5.1.2

Solvents Used in Analysis

SOLVENTS	GRADE	USED IN
1-4 Dioxane	Reagent	Gravimentric Analysis
Methanol	"	Gravimentric Analysis
Methanol	"	Spectrophotometry
Chloroform	"	Spectrophotometry
Tetrahydrofuran	"	G.P.C.
Sulphuric Acid	"	Fricke Dosimetry
NACL	"	Fricke Dosimetry
Ferrous Amonium Sulphide	"	Fricke Dosimetry
Terphenyl	"	Heating Bath

with the heat transfer medium, terphenyl. For a normal experimental run, the vials were put in place, and the radiation source positioned with remote handling slave manipulators. At predetermined time intervals the samples were taken out of the radiation field and put in a shielded ice bath. Then the Co^{60} source was temporarily retracted while the vials were exchanged and then the process was restarted. Samples were polymerized thermally and also by a combination of thermal and radiation reaction. The latter polymerizations were conducted at two different dose rates.

5.3 Analysis

5.3.1 G.P.C.

Some of the samples were analyzed by gel permeation chromatography. The data were read directly from the chromatograph in digital form and processed on the CDC 6400 Computer (See Appendix A.4). Peak elution heights for each sample were obtained to the nearest 0.05 of an elution count and $\bar{M}_n$, $\bar{M}_W$ were found with the assumption of infinite resolution. The results are not corrected for imperfect resolution.

5.3.2 Gravimetry

For conversions of styrene monomer up to about 95%, the determination of conversion was done gravimetrically. The polymer sample was weighed, dissolved in 1-4 Dioxane and was poured very slowly into a ten-fold excess methanol. The precipitated polymer was filtered on fine porous glass crucibles, dried under vacuum and weighed.

The amount of dried polymer, expressed as a percentage in the total weight of polymer sample gave the percent conversion.

5.3.3 Ultraviolet Spectrophotometry

U.V. Spectrophotometry was employed in the determination of conversion above 95% with a demonstrated accuracy of better than 0.1%. Accurately weighed samples of approximately 0.12 grams of each polymer were dissolved in chloroform and polystyrene precipitated in methanol. The clean filtrate containing unreacted styrene was used for the measurement of absorbance at 245 μm by a Beckman Model DK-1 Spectrophotometer. Percentage conversion was then calculated from the calibration curve of absorbance versus styrene concentration.

CHAPTER 6

EXPERIMENTAL CONDITIONS AND RESULTS

6.1 Effects of Variables on the Experimental Results

Since 1839 when Edward Simonin first converted styrene to polystyrene and called it 'Styrol Oxide' the subject of styrene polymerization has been advanced by a surprisingly large number of individuals.

The amount of knowledge gained is not only abundant but also highly specific and exact--the kind of information that is necessary for the making of polystyrene into an attractive, useful and marketable plastic. The polymerization reaction is affected by many variables, some of which will be discussed as background for our experimental plan.

6.1.1 Purity of Reagents

Small quantities of impurities can exert a powerful influence on radiation-induced reactions. In purely organic systems, 'energy transfer' effects of various kinds can take place, so that minor constitutents can assume a disproportionate importance.

In the course of styrene polymerization, one of the most important matters of concern is the purity of styrene monomer. As is the case with most of the plastic monomers, this material is quite active and unless proper steps are taken, the properties of the product are significantly effected.

Styrene monomer now commercially available analyzes better than 99.5%, the major impurity being ethyl benzene and water. Minor impurities include parts per million of chloride, sulfur, aldehydes, divinylbenzene, peroxides, phenyl acetylene and polymer. The large scale production of extremely pure styrene monomer represents a technical achievement of remarkable significance in view of the reactive nature of styrene toward polymerization. Further attempts to purify styrene monomer frequently lead to disappointing results, especially when the work is carried out on a small scale. For all practical purposes, the foreign substances exert only a minor influence on the course of polymerization. Nevertheless, for a careful research work it may be desirable to trace these effects in some cases, and in general, it may account for many peculiarities which accompany the polymerization of styrene.

The polymerization of styrene is a chain reaction in which one styrene molecule becomes activated, picks up another styrene molecule, which in turn picks up a third, etc (14, 16, 32, 43, 55, 67). In this manner a long-chain molecule containing perhaps as many as a thousand monomer units can be formed in a small fraction of a second. The chain finally stops growing for one or more reasons. It has frequently been found that impurities are very efficient chain stoppers and since one molecule of an impurity could conceivably terminate a chain containing a thousand monomer units, it is understandable that small amounts of impurities may influence molecular weight considerably. Because of the chain nature of polymerization reaction, it is rather difficult to assign definite roles to the various impurities which have been detected in styrene monomer. The following outline identifies sources of trouble which result from impurities.

AIR (OXYGEN):

One important impurity which affects nearly every radiation induced reaction is air. Molecular oxygen is shown to be an effective inhibitor by Kolthoff et al (49) and has been demonstrated to account for much of the induction period for polymerizations carried out in the presence of oxygen. Also there are some reasons to believe that the so-called thermal polymerization of styrene without addition of catalyst is chiefly caused by the presence of small amounts of peroxides formed by the reaction of styrene with dissolved oxygen (62, 67). It is also suggested that oxygen in the polymer chain constitutes a weak link, facilitating thermal degradation of polystyrene (11). More detail can be found in (39).

ETHYL BENZENE

The molecular weight of polystyrene will be depressed markedly by the presence of a large amount of ethyl benzene. The evaporation of small amounts of this impurity from polystyrene may promote crazing or blushing. For further detail the reader is referred to (67).

DIVINYLBENZENE

Presence of more than 0.04% of this material in styrene will form crosslink polymer which tends to be insoluble (51).

WATER

The manner in which water in styrene monomer affects its polymerization has not been fully determined. Styrene monomer as supplied normally contains from 80 to 200 PPM of water, although direct contact with water or exposure to air of high humidity will raise the moisture content to an equilibrium water content of styrene at various temperatures (22). There is some indication that a small amount of water soluble in the monomer may produce a slight haziness in the polymer formed and impair the good electric properties of polystyrene. If the monomer is stored at lower than room temperature the container should be warmed to ambient temperature before the opening in order to avoid the absorption of water by cold styrene.

ALDEHYDES

Styrene on exposure to air rapidly forms certain aldehydes and ketones. Styrene containing these does not behave like high-purity type styrene. There is a marked difference in the rate of polymerization and in the induction period which precedes it. These oxidation products have significant dipole moments, so that the dielectric constant of the monomer and polymer formed is not as low as the higher purity material. Also, it has been observed that the presence of aldehydes will promote the attack of styrene monomer on metals, especially copper and brass. They can also oxidize to peroxides during polymerization. Discolouration and lowering of the molecular weight of polymer can be counted as some other effects of aldehydes (62).

POLYMERS

There is no existing evidence to indicate that the presence of small amounts of polymer in the styrene monomer interferes with subsequent polymerization. In fact, a common practice in some applications is to dissolve polystyrene in styrene monomer so as to reduce shrinkage and heat evolution during polymerization. But in any kinetics measurement such as the determination of the initial rate of polymerization or percent conversion the amount of polymer initially present in the system should be known accurately.

PEROXIDES

These materials are usually good polymerization catalysts and some of the variations in the rate of polymerization from one sample of monomer to another may be attributed to this impurity. Most peroxide catalysts are decomposed at elevated temperatures, liberating carbon dioxide. This is offered as an explanation for some of the bubbles occasionally observed in polystyrene (these bubbles were observed in samples polymerized at 180°C and 200°C in this work).

PHENYL ACETYLENE

In the early days of styrene manufacture, phenyl acetylene was frequently present to the extent of 2 or 3%. Titrations on such styrene would therefore show over 100% because of the extra bond in phenyl acetylene molecules. This compound has been identified as a fairly active polymerization inhibitor for styrene (46).

As it is mentioned in (22) this substance also can be formed at very high temperatures as a result of dehydrogenation of styrene or disproportionation of two moles of styrene. In the present work the effects of phenyl acetylene were observed in polymerization of styrene at 200°C and will be discussed in a later chapter of this report. However, present day styrene monomer will contain only a few PPM (4 to 5 PPM) of this impurity.

SULFUR

Free sulfur may sometimes occur in styrene monomer because of its use during distillation. Even a few PPM of sulfur produces an easily measurable reduction in molecular weight and a marked impairment in the light stability of the resulting polystyrene. However organic sulfur compounds which are present in small amounts in styrene has a relatively slight influence on polymerization of styrene (51).

CHLORIDES

The presence of any chloride traces in styrene monomer could probably be counted as a result of aluminum chloride catalyst used in Friedel and Craft's reaction in the manufacture of ethyl benzene. Any chloride present is probably in the ring and while there are no known effects that can be traced directly to chloride in the ring, chlorides in the side chain do tend to affect polymerization. So it seems advisable to keep the chloride content in monomer to a minimum.

Based on all of the above considerations one has to be careful about the amounts and types of different impurities present in styrene monomer which can be used for different areas of research and investigations.

6.1.2 Pressure and Temperature Effects

6.1.2.1 Pressure Effects

Since the polymerization of styrene involves a reduction in specific volume it might be anticipated that pressure would accelerate the reaction. The data which has been published by Gillham (50) indicate a 15-fold increase in rate accompanied by a 1.7-fold increase in molecular weight on going to 4000 atmospheres at 100°C. Similar results were obtained in suspension polymerization-- a 50% increase in rate up to 1000 atmospheres. The following Antoine-Type equation can be used for the calculation of styrene vapour pressure at different temperatures (22).

$$\log_{10} P_{M.M.Hg} = 6.95711 - 1445.58/(t+209.43)$$

Table 6.1.2.1 shows a series of vapour pressures at different temperatures.

6.1.2.2 Temperature Effects

One of the most significant factors in the polymerization of styrene monomer is temperature. Temperature effects on numerous polymerization techniques have been investigated for a long time and the literature is crowded with numerous papers and results concerning these effects.

In thermally-initiated polymerizations changes in temperature will affect the initiation, propagation and termination stages (32).

TABLE 6.1.2.1

Styrene V.P. at Different Temperatures

Temperature °C	V.P. of Styrene Monomer at indicated temperatures M.M.Hg
150	861.5
155	978.2
160	1115
165	1248
180	1758
200	2669

Increase in temperature gives rise to an increased number of primary radicals, it also increase the rate of polymerization, but it may lead to a reduced average molecular weight (42). In some special cases if the temperature rises the rate of polymerization increases but the change in molecular weight will be independent of rate of polymerization--that is independent of change in temperature (emulsion polymerization). Furthermore, even the physical and chemical behaviour of polymer will be dependent on the temperature at which polymerization was conducted. For any kinetics study one has to trace the changes in temperature during the course of polymerization and this leads to the use of proper and accurate methods for temperature measurements.

Because the styrene polymerization reaction is exothermic, it behaves much like auto-catalytic reactions. A temperature rise accelerates the rate of polymerization which in turn liberates heat and further raises the temperature. This can result in a runaway reaction with resulting high temperatures and accompanying high pressure. More detail about the effects of temperature on polymerization of styrene monomer can be found in the literature review of this report.

6.1.3 Geometry of Reactor

The study of the kinetics of styrene polymerization has to be accomplished in an isothermal condition. Since the reaction is an exothermic one, thus the geometry of the reactor is very important from the point of heat dissipation.

It is well known that styrene and polystyrenehave a very low thermal conductivity. In order to achieve the isothermal conditions in reaction vials, one has to choose the optimum size consistent with the highest rate of heat dissipation and this can be fulfilled by conducting the experiments in a vial of smallest possible diameter. A large diameter vial might give a misleading result due to inconsistency in reaction temperature measured and actual temperature at which the reaction has taken place. More details about the size of vial can be found in the Appendices of this report and (5).

6.1.4 Methods of Analysis

6.1.4.1 Gravimetric Method

This method has been recommended by most of the workers in this field (14, 15, 16, 18, 51). The method is intended to determine appreciable quantities of polymer in styrene monomer. A complete procedure can be found in Appendix A.4 of this report. The efficiency of this method is good for the percentage of conversion up to 95%. Beyond this limit the accuracy of the method is doubtful.

The only inefficiency which has been observed with this method in the present study was inaccuracy of the results at very low conversions. The solubility of low molecular weight polystyrene, such as dimer, trimer, tetramer etc., in the methanol could be one of the reasons. The overall accuracy of this method can be considered in between (± 0.5% to ± 1.5% conversion).

6.1.4.2 U.V. Spectrophotometric Method

Conversion beyond 95% was measured by ultraviolet spectrophotometric methods. The absorbance of samples were read at 245 mμ and then converted to concentration by use of a calibration curve (57) and Figure A.5.3.1. Because of the high degree of sensitivity the ultraviolet absorption method is particularly useful for the determination of extremely small amount of styrene monomer in polymer samples. It has been claimed that by this method it is possible to detect the styrene monomer in concentrations as low as 0.00001% (51), which seems extreme. The precision of this method is better than 0.1%. Full details are given in Appendix A.5.

6.1.4.3 Fricke Dosimetry

The intensity of radiation was measured by this technique. Samples of ferrous ammonium sulfate were irradiated for a definite amount of time and the absorption due to ferric ions in the irradiated samples was measured at 304 mμ by a U.V. spectrophotometer. The relationship between dosage and optical absorption of the solution is given in Appendix B.2.

Extreme precautions were taken in order to avoid the very probable errors due to contaminations. The results are subject to about ± 5% error.

6.1.4.4 G.P.C. Analysis

Gel permeation chromatography was used for the determination of weight average molecular weight and number average molecular weight.

This method is one of the most rapid and accurate techniques for molecular weight determinations and has been used by numerous investigators (e.g., 14, 18, 52). Twenty-eight samples were analyzed of which 10 were done in the department's G.P.C. and 18 in the laboratories of Polymer Corporation at Sarnia. The results are different because of the difference in column packing materials. The accuracy of the results can be counted in the range of ± 10 to ± 15%. For more explanations and method of analysis the reader is referred to Appendix C.1 and (18, 52).

6.1.5 General Conditions of Experiments

(a) Purity of Reagents

Styrene monomer was supplied by Polymer Corporation, Sarnia, Ontario. No further purifications were made since it was planned to apply the results to conventional industrial techniques. Reagent grade solvents and solutes were used in all experiments. The complete list of solvents, solutes and impurity of styrene monomer is given in Tables 5.1.1 and 5.1.2 of this report.

(b) Temperature

The experiments were conducted at six different temperatures as follows: 150°C, 155°C, 160°C, 165°C, 180°C and 200°C. The temperature of the oil bath was recorded by 4 thermocouples simultaneously. These four thermocouples were located around the sample holder in the oil bath and the temperature registered on a recording potentiometer. In this way the temperature outside the vials was measured to an accuracy better than ± 0.3°C.

(c) Dose Rates

Most of the experiments were carried out at two different dose rates of 51 and 20 Rads/sec., by positioning the vials at two different slots in the sample holder. These slots were at a distance of $3\frac{3}{8}$ inches and 6 inches from the axis of the source.

(d) Vial Size

Almost all of the experiments were carried out in a vial size of 7 MM outside diameter. Each vial was filled up to 3 inches and sealed at 4 inches under 10^{-6} mm H.g. vacuum.

Over 350 samples were prepared, polymerized and have been analyzed by different methods

6.2 Sample Designation

The designations for thermal polymerized samples are composed of 3 parts, and the radiation polymerized samples have a four-part identification. Each part of the number shows a different specification for the experiment. The characters are shown in Table 6.2.1.

EXAMPLES

Sample No. A1R18 means this sample was irradiated at 200°C with a dose rate of 51 Rads/sec. and has the sequence number of 18 in the conversion time table.

TABLE 6.2.1

Sample Designation

CHARACTER	POSITION	MEANING
A	First	200°C
B	First	180°C
C	First	165°C
D	First	160°C
E	First	155°C
F	First	150°C
R	Third	Radiated Sample
T	Second	Thermal Polymerized Sample
1	Second	Dose Rate of 51 Rads/sec.
2	Second	Dose Rate of 20 Rads/sec.

Sample No. DT12 means this sample was a thermal polymerized sample at 160°C and has a sequence number of 12 in the conversion time table. So as it can be noted, in any sample number the first character is temperature designation, 2nd character for dose rate, 3rd character for thermal polymerized or radiation polymerized designation, and the 4th character which will be a number would show the sequence number in conversion time tables.

6.3 Conversion Time Data of Thermal Polymerized Samples

Nearly half of the samples were used for thermal polymerization studies at indicated temperatures. Percent conversion was obtained by the use of gravimetric (below 90% conversion) and spectrophotometric (beyond 90% conversion) techniques of analysis. The results of this set of experiments are shown in Tables 6.3.1, 6.3.2, 6.3.3 and 6.3.4, respectively.

6.4 Conversion Time Data of (Radiation + Thermal) Polymerized Samples

Tables 6.4.1 to 6.4.10 will show the results of samples polymerized with two different dose rates and at indicated temperatures.

TABLE 6.3.1

Conversion Time Data for Thermal Polymerized at [160°C ± 0.2°C]

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
DT1	2	5.1	2.6
DT2	4	9.1	2.3
DT3	8	15.7	1.9
DT4	12	21.8	1.8
DT5	18	30.8	1.7
DT6	24	39.1	1.6
DT7	30	42.3	1.4
DT8	40	53.5	1.3
DT9	60	67.5	1.1
DT10	90	79.5	0.9
DT11	120	85.2	0.7
DT12	180	93.8*	0.5
DT13	240	95.3*	0.4
DT14	300	96.2*	0.32
DT15	360	96.4*	0.3
DT16	420	97.3*	0.2

* % Conversion obtained by U.V. spectrophotometric method

TABLE 6.3.2

Conversion Time Data for Thermal Polymerized
At 165°C ± 0.2°C

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
CT1	2	8.9	4.4
CT2	3	12.3	4.1
CT3	4.2	14.6	3.5
CT4	6	18.9	3.1
CT5	8	22.5	2.8
CT6	12	28.6	2.4
CT7	18	-	-
CT8	24	45.6	1.9
CT9	30	-	-
CT10	40	75.1	1.88
CT11	60	89.6	1.5
CT12	90	92.2*	1.0
CT13	120	94.3*	0.8
CT14	180	96.7*	0.5
CT15	240	97.9*	0.4
CT16	300	98.4*	0.3

* % Conversion obtained by U.V. spectrophotometric technique

TABLE 6.3.3

Conversion Time Data for Thermal Polymerized At 180°C ± 0.2°C

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
BT1	2	13.3	6.6
BT2	4	21.2	5.3
BT3	8	34.7	4.3
BT4	12	46.3	3.9
BT5	18	58.3	3.2
BT6	24	67.4	2.8
BT7	30	74.1	2.5
BT8	40	80.0	2.0
BT9	60	86.5	1.4
BT10	90	90.4	1.0
BT11	120	94.1*	0.8
BT12	190	95.5*	0.5
BT13	240	96.2*	0.4
BT14	300	97.1*	0.32
BT15	360	98.0*	0.30
BT16	421	98.5*	0.2

* % Conversion obtained by U.V. spectrophotometric technique

TABLE 6.3.4

Conversion Time Data for Thermal Polymerized
At 200°C ± 0.2°C

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
AT1	1	7.0	7.0
AT2	1.5	12.6	8.4
AT3	2	17.1	8.5
AT4	2.5	23.3	9.3
AT5	3.0	27.0	9.0
AT6	4	34.8	8.7
AT7	5	41.4	8.2
AT10	8	56.3	7.0
AT11	9	59.1	6.6
AT13	12	67.2	5.6
AT15	16	77.1	4.8
AT17	24	83.7	3.5
AT18	30	90.3	3.0
AT19	40	89.1	2.2
AT20	50	90.9	1.8
AT21	60	93.6*	1.6
AT22	90	97.0*	1.1
AT23	120	98.0*	0.8
AT24	180	99.0*	0.6
AT25	240	99.2*	0.4

* % Conversion obtained by U.V. Spectrophotometric Technique

TABLE 6.4.1

Conversion Time Data of R.+T. Polymerized at
Dose Rate = 51 Rads/Sec. & 20 Rads/Sec.
(150°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
F1R1	2	3.0	1.5
F1R2	4.2	7.4	1.7
F1R3	6.2	11.4	1.8
F1R4	8	12.0	1.5
F2R1	2	3.1	1.6
F2R2	4	7.2	1.8
F2R3	6	10.0	1.6
F2R4	8	12.0	1.5

TABLE 6.4.2

Conversion Time Data of R.+T. Polymerized at Dose Rate = 51 Rads/Sec. & 20 Rads/Sec. (155°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
E1R1	2	4.0	2
E1R2	4	8.5	2.1
E1R3	6	11.5	1.9
E1R4	8	14.1	1.8
E2R1	2	3.8	1.9
E2R2	4	9.3	2.1
E2R3	6	11.5	1.9
E2R4	8	14.0	1.8

TABLE 6.4.3

Conversion Time Data of R.+T. Polymerized at
Dose Rate = 51 Rads/Sec.
(160°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
D1R1	2	5.8	2.9
D1R2	4	10.8	2.7
D1R3	8	16.8	2.1
D1R4	12	22.1	1.8
D1R5	18	30.0	1.7
D1R6	24	38.5	1.6
D1R7	30	45.8	1.5
D1R8	40	54.0	1.4
D1R9	60	68.5	1.1
D1R10	90	90.2*	1.0
D1R11	120	96.4*	0.8
D1R12	180	99.2*	0.6
D1R13	240	99.9*	0.4
D1R14	300	99.93*	0.33
D1R15	360	100.0*	0.30
D1R16	420	100.0*	0.2

* % Conversion obtained by U.V. spectrophotometric technique

TABLE 6.4.4

Conversion Time Data of R.+T. Polymerized at
Dose Rate = 20 Rads/Sec.
(160°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
D2R1	2	5.75	2.9
D2R2	4	10.8	2.7
D2R3	8	16.7	2.1
D2R4	12	22.2	1.9
D2R5	18	32.1	1.8
D2R6	24	38.0	1.6
D2R7	40	55.4	1.4
D2R8	60	68.0	1.1
D2R9	90	90.8*	1.0
D2R10	120	96.3*	0.8
D2R11	180	99.2*	0.6
D2R12	240	99.91*	0.4
D2R13	300	99.92*	0.33
D2R14	360	99.95*	0.30
D2R15	420	100.0*	0.20

* %Conversion obtained by U.V. spectrophotometric technique

TABLE 6.4.5

Conversion Time Data of R.+T. Polymerized at
Dose Rate = 51 Rads/Sec.
(165°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
C1R1	2	8.8	4.4
C1R2	3	12.5	4.1
C1R3	4.2	14.5	3.5
C1R4	6	18.9	3.1
C1R5	8	22.6	2.8
C1R6	12	29.7	2.5
C1R7	18	36.9	2.1
C1R8	24	47.6	2.0
C1R9	30	56.8	1.9
C1R10	40	75.1	1.88
C1R11	60	93.4*	1.6
C1R12	90	98.8*	1.1
C1R13	120	98.8*	0.8
C1R14	180	99.6*	0.6
C1R15	240	99.8*	0.4
C1R16	300	99.9*	0.33
C1R17	360	99.91*	0.3

* % Conversion obtained by U.V. spectrophotometric technique

TABLE 6.4.6

Conversion Time Data of R.+T. Polymerized at
Dose Rate = 20 Rads/Sec.
(165°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
C2R1	2	8.9	4.4
C2R2	3	12.3	4.1
C2R3	4	14.6	3.6
C2R4	7.8	21.9	2.8
C2R5	8	22.3	2.8

TABLE 6.4.7

Conversion Time Data of R.+T. Polymerized at
Dose Rate = 51 Rads/Sec.
(180°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
B1R1	2	13.1	6.6
B1R2	4	21.4	5.3
B1R3	8	33.9	4.2
B1R4	12	45.9	3.8
B1R5	18	57.6	3.2
B1R6	24	67.4	2.8
B1R7	30	74.6	2.5
B1R8	40	80.9	2.0
B1R9	60	91.6*	1.5
B1R10	90	96.2*	1.1
B1R11	120	98.3*	0.8
B1R12	190	99.4*	0.5
B1R13	270	99.5*	0.4
B1R14	300	99.7*	0.33
B1R15	360	99.8*	0.30

* % Conversion obtained by U.V. spectrophotometric technique

TABLE 6.4.8

Conversion Time Data of R.+T. Polymerized at
Dose Rate = 20 Rads/Sec.
(180°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
B2R1	2	13.2	6.6
B2R2	4	21.3	5.3
B2R3	8	34.3	4.3
B2R4	11.6	44.4	3.8
B2R5	18	58.6	3.3
B2R6	24	67.2	2.8
B2R7	30	74.3	2.5
B2R8	40	80.5	2.0
B2R9	60	91.5*	1.5
B2R10	90	95.5*	1.1
B2R11	120	98.1*	0.8
B2R12	190	99.4*	0.5
B2R13	270	99.5*	0.4
B2R14	300	99.75	0.33
B2R15	360	99.9*	0.3

* % Conversion obtained by U.V. spectrophotometric technique

TABLE 6.4.9

Conversion Time Data of R.+T. Polymerized at Dose Rate = 51 Rads/Sec. (200°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min.)
A1R1	1	7.3	7.3
A1R2	1.5	12.0	8.0
A1R3	2	17.0	8.5
A1R4	2.5	22.3	8.9
A1R5	3	26.9	9.0
A1R6	4	35.4	8.9
A1R7	5	41.7	8.3
A1R8	6	45.7	7.6
A1R9	7	52.7	7.5
A1R10	8	56.7	7.1
A1R11	9	59.9	6.7
A1R12	10	63.1	6.3
A1R13	12	67.3	5.6
A1R14	14	70.4	5.0
A1R15	16	74.4	4.7
A1R16	18	75.2	4.2
A1R17	24	83.1	3.9
A1R18	30	87.4*	2.9
A1R19	40	93.2*	2.3
A1R20	50	96.8*	1.9
A1R21	60	99.3*	1.7
A1R22	90	99.4*	1.0
A1R23	120	99.5*	0.8
A1R24	180	99.7*	0.6
A1R25	240	99.8*	0.4

* % Conversion obtained by U.V. spectrophotometric technique

TABLE 6.4.10

Conversion Time Data of R.+T. Polymerized at
Dose Rate = 20 Rads/Sec.
(200°C ± 0.2°C)

SAMPLE NO.	TIME (Min.)	% CONVERSION	RATE (%/Min).
A2R1	1	7.7	7.7
A2R2	2	17.6	8.8
A2R3	3.7	34.3	9.3
A2R4	6	46.6	7.8
A2R5	10	65.8	6.6
A2R6	16	77.1	4.8
A2R7	24	82.1	3.4
A2R8	30	86.3*	2.9
A2R9	40	94.1*	2.3
A2R10	50	96.8*	1.9
A2R11	60	99.2*	1.7
A2R12	98	99.3*	1.0
A2R13	122	99.5*	0.8
A2R14	180	99.7*	0.6
A2R15	240	99.8*	0.4

* % Conversion obtained by U.V. spectrophotometric technique

6.5 Initial Rates of Reaction for Thermal and (Radiation plus Thermal) Polymerized Samples

Initial rates of reaction at different temperatures and dose rates were obtained in (%/Min.) for conversions up to 10%.

These initial rates are the average of rates of reaction in %/Min. of a number of samples which have conversions below 10%. The results are shown in Table 6.5.1.

TABLE 6.5.1

Initial Rate of Reaction %/Min.

Temp. °C	Average Initial T. Rate %/Min.	Average Initial R.+T. Rate %/Min. 51 Rads/Sec.	Average Initial R.+T. Rate %/Min. 20 Rads/Sec	No. of Points Used
150	1.17*	1.6	1.6	3
155	1.6*	2.0	1.96	3
160	2.5	2.8	2.8	2
165	4.3	4.3	4.3	2
180	6.6	6.6	6.6	2
200	7.7	7.7	7.7	2

* Data obtained from Figure 7.1g Page 220 of Boundy & Boyer.

At 200°C the presence of phenyl acetylene probably caused some induction period which consequently reduced the initial rate of polymerization. This special section will be discussed in detail in the 'Discussion of the Results' section.

6.6 Polymerization Rate Curves for Different Temperatures

The general features of thermal (T.) and radiation + Thermal (R.+T.) polymerized styrene monomer are shown in Figures 6.6.1, 6.6.2, 6.6.3, and 6.6.4, wherein the amount of styrene polymerized has been plotted as a function of time at several temperatures using the data of previous tables.

These polymerization rate curves exhibit two distinct phases, the nature of which are determined by the polymerization conditions. The first phase is a period of rapid polymerization at the beginning of the reaction which persists almost to the end of the reaction and for which the rate is exponentially dependent upon temperature. The second phase represents slowing down in rate as the reaction approaches completion and the monomer becomes exhausted.

The rate of polymerization varied with conversion from the early stage up to complete conversion. Figures 6.6.5, 6.6.6, 6.6.7, 6.6.8, 6.6.9, 6.6.10, 6.6.11 and 6.6.12 show this variation, for different temperatures, both radiated and thermal polymerized samples.

6.7 G.P.C. Data

Weight average and number average molecular weights ($\bar{M}_W$, $\bar{M}_N$) of thermal and (Radiation + Thermal) polymerized samples are shown in Section C.6 of the Appendices.

The effect of temperature on molecular weight of styrene polymerized by thermal and radiation + thermal is shown in Figure 6.7.1

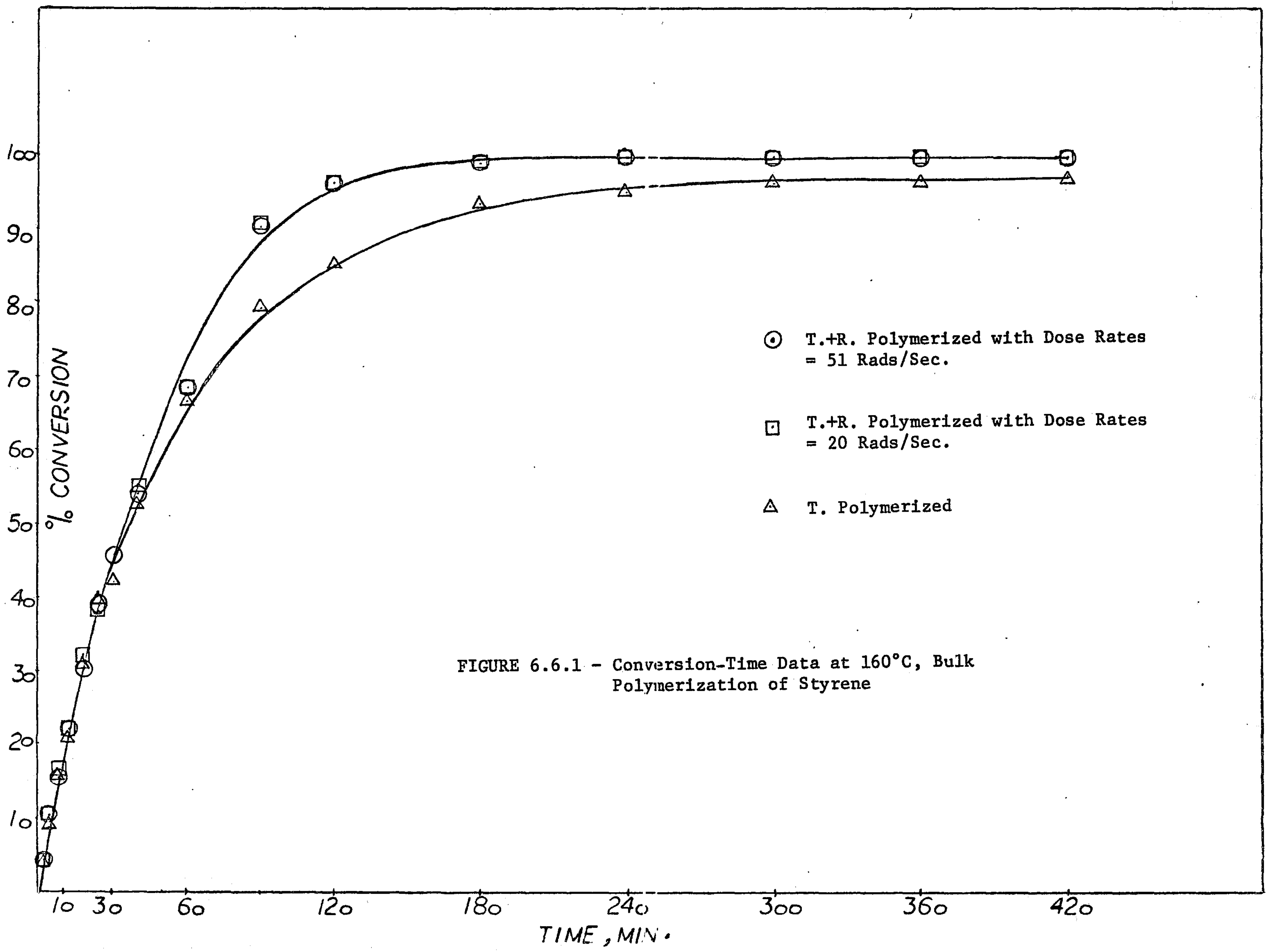


FIGURE 6.6.1 - Conversion-Time Data at 160°C, Bulk Polymerization of Styrene

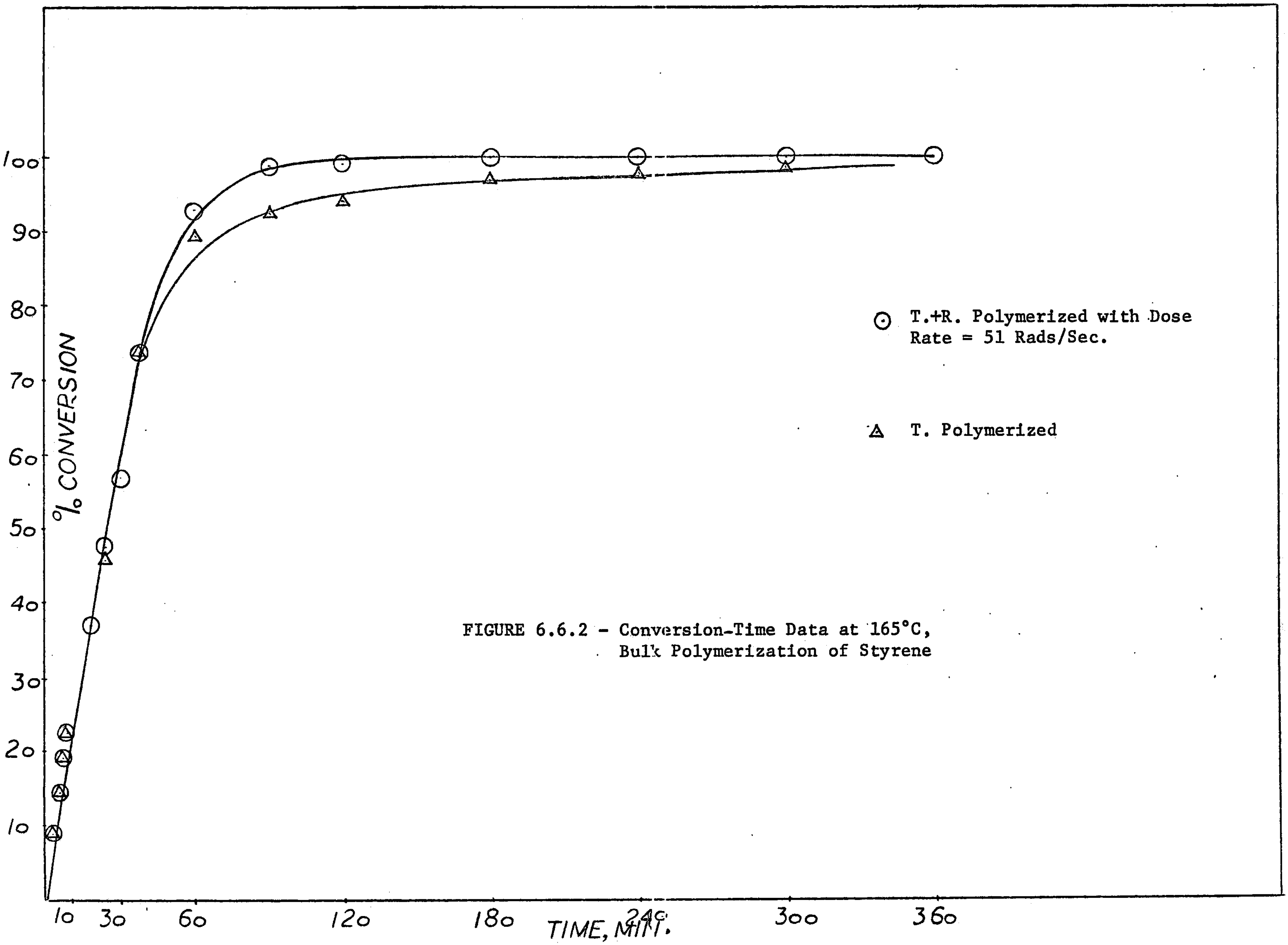


FIGURE 6.6.2 - Conversion-Time Data at 165°C, Bulk Polymerization of Styrene

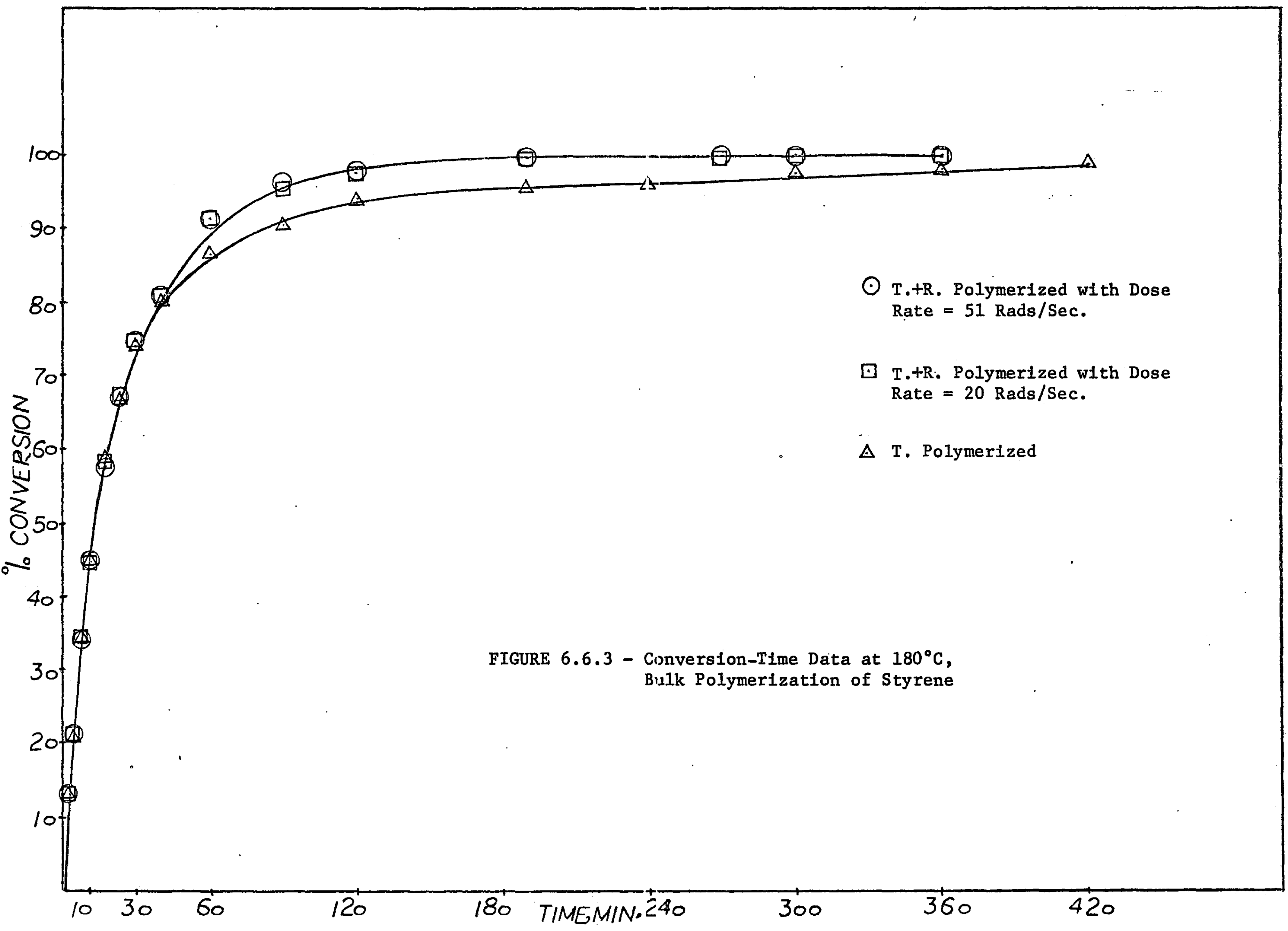


FIGURE 6.6.3 - Conversion-Time Data at 180°C, Bulk Polymerization of Styrene

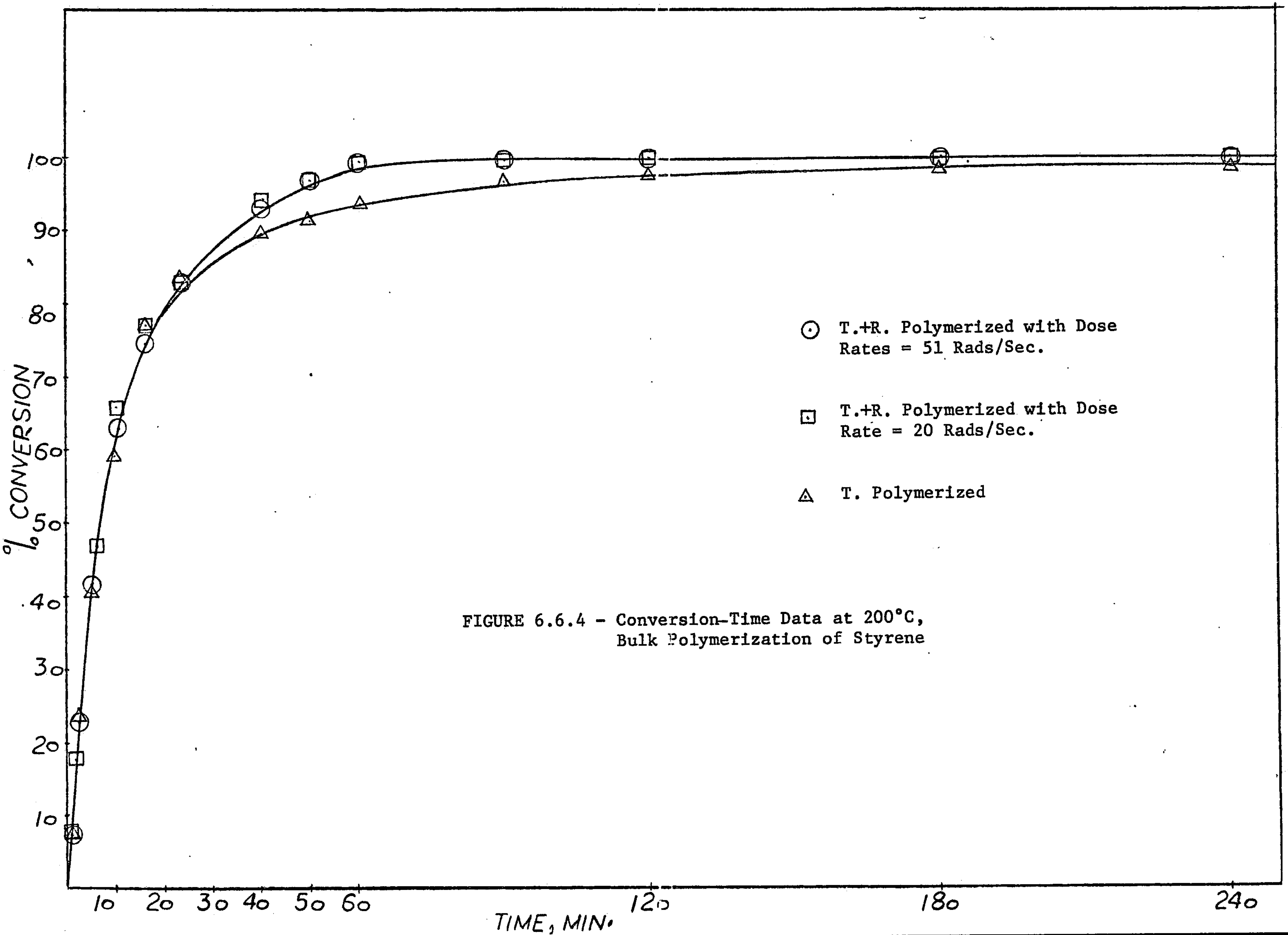


FIGURE 6.6.4 - Conversion-Time Data at 200°C, Bulk Polymerization of Styrene

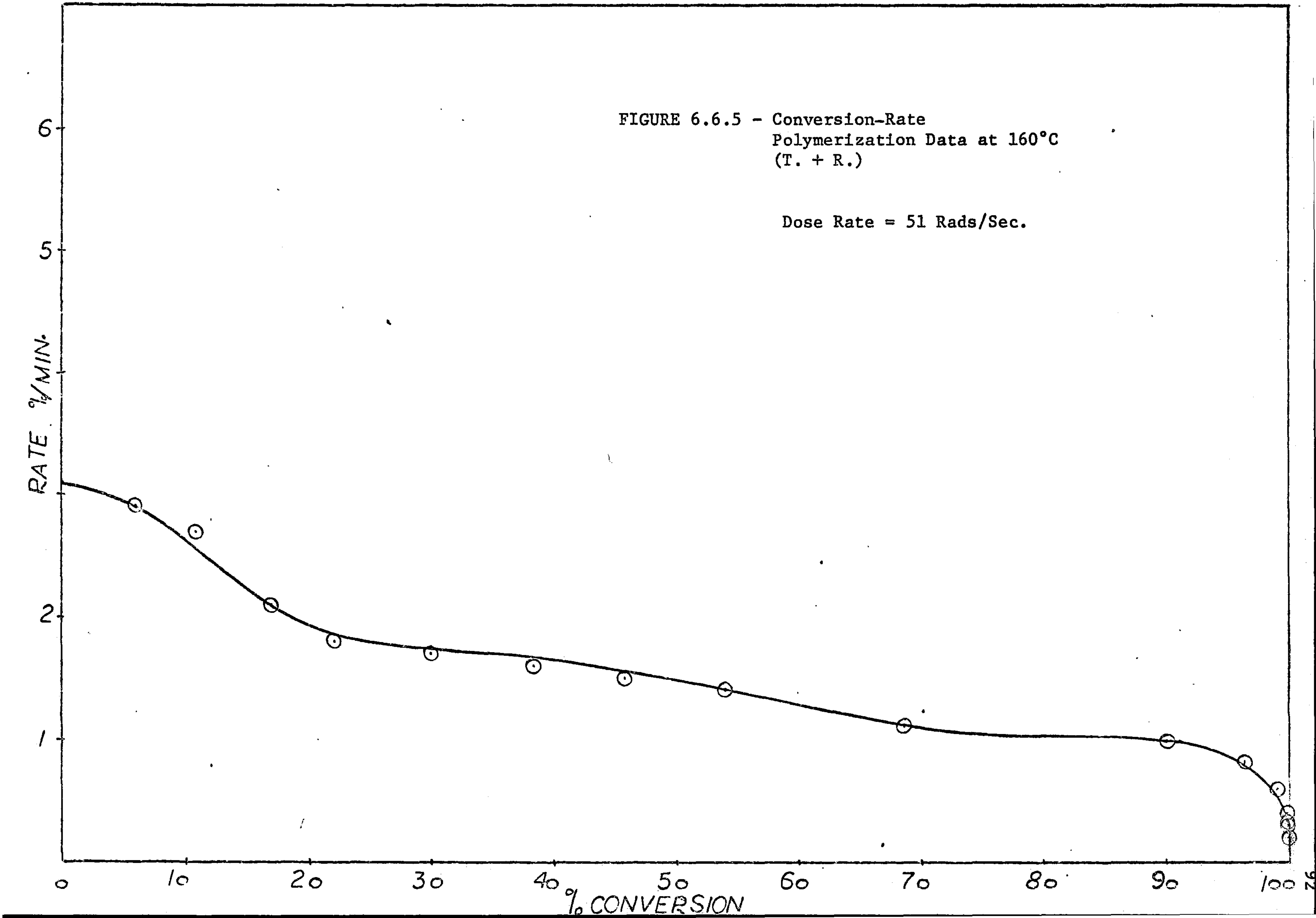


FIGURE 6.6.5 - Conversion-Rate
Polymerization Data at 160°C
(T. + R.)

Dose Rate = 51 Rads/Sec.

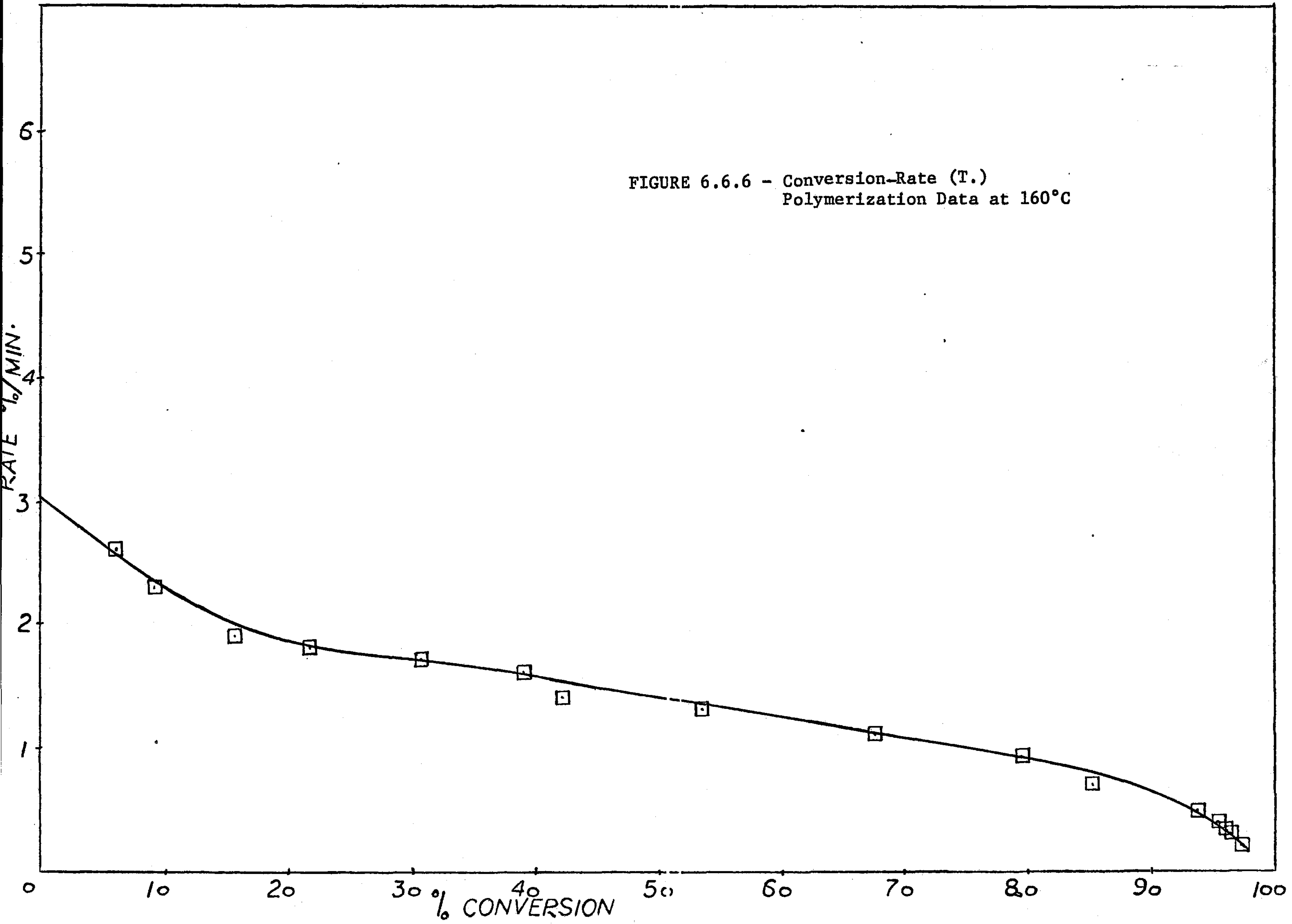


FIGURE 6.6.6 - Conversion-Rate (T.)
Polymerization Data at 160°C

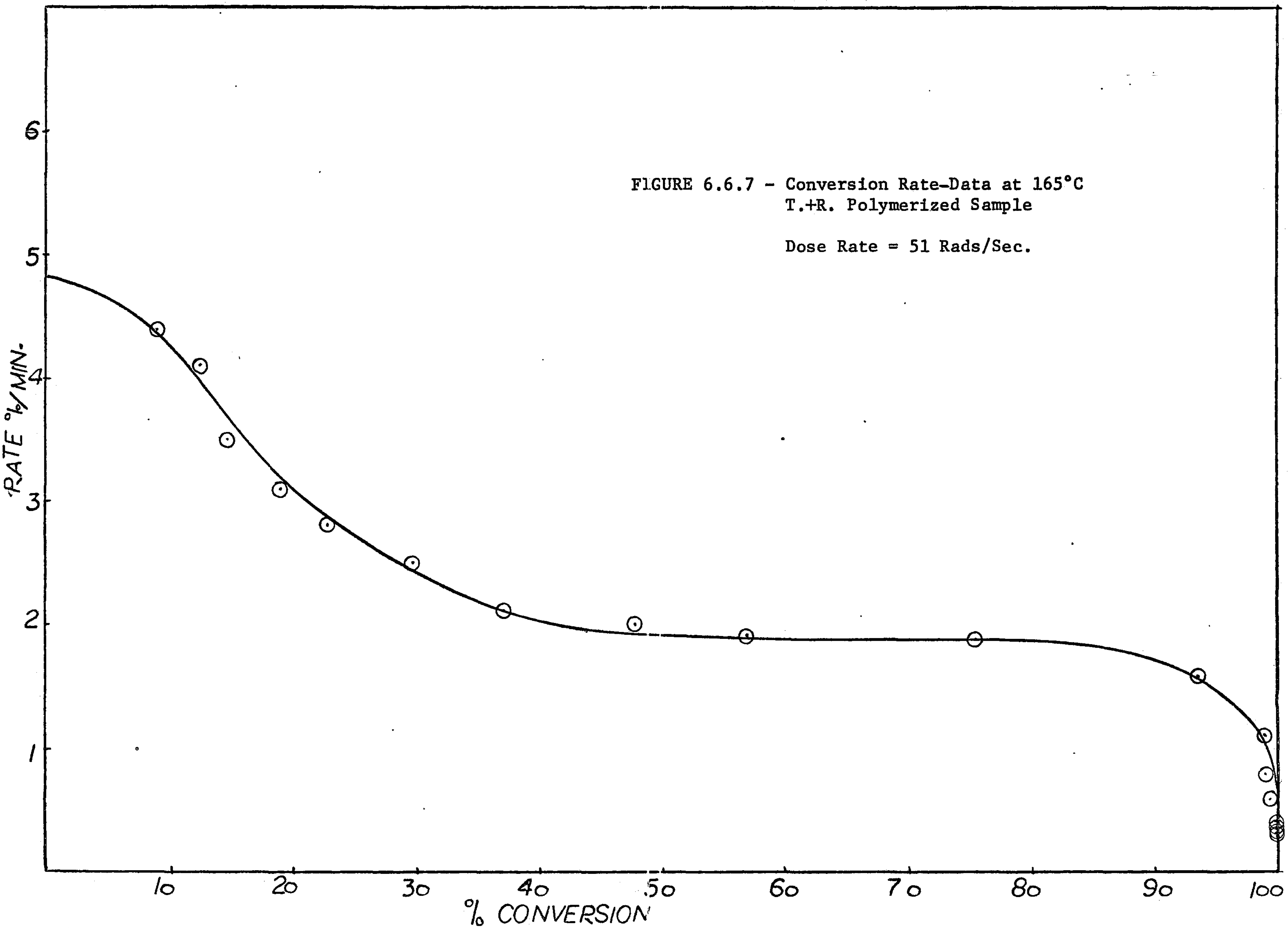


FIGURE 6.6.7 - Conversion Rate-Data at 165°C
T.+R. Polymerized Sample

Dose Rate = 51 Rads/Sec.

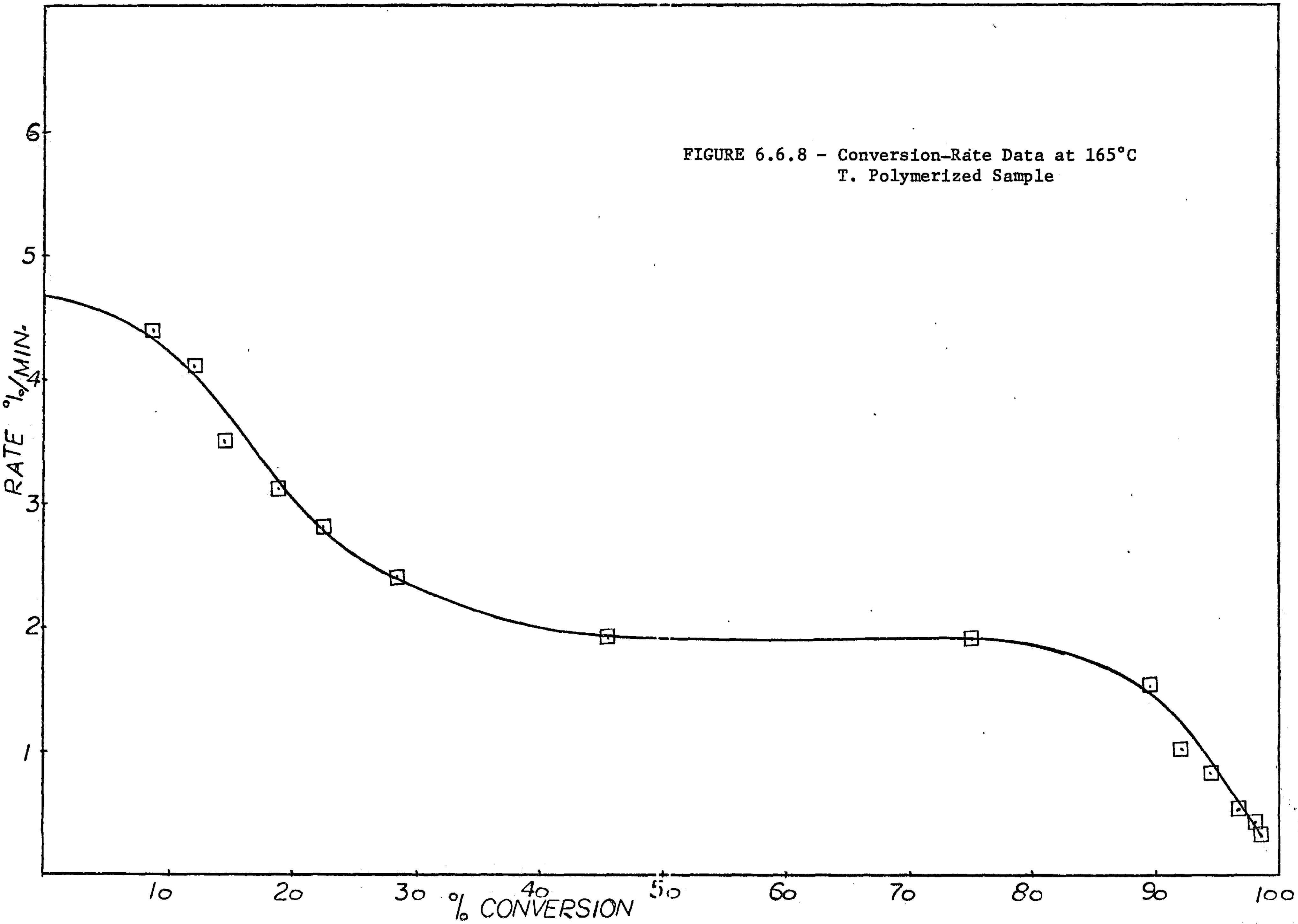


FIGURE 6.6.8 - Conversion-Rate Data at 165°C
T. Polymerized Sample

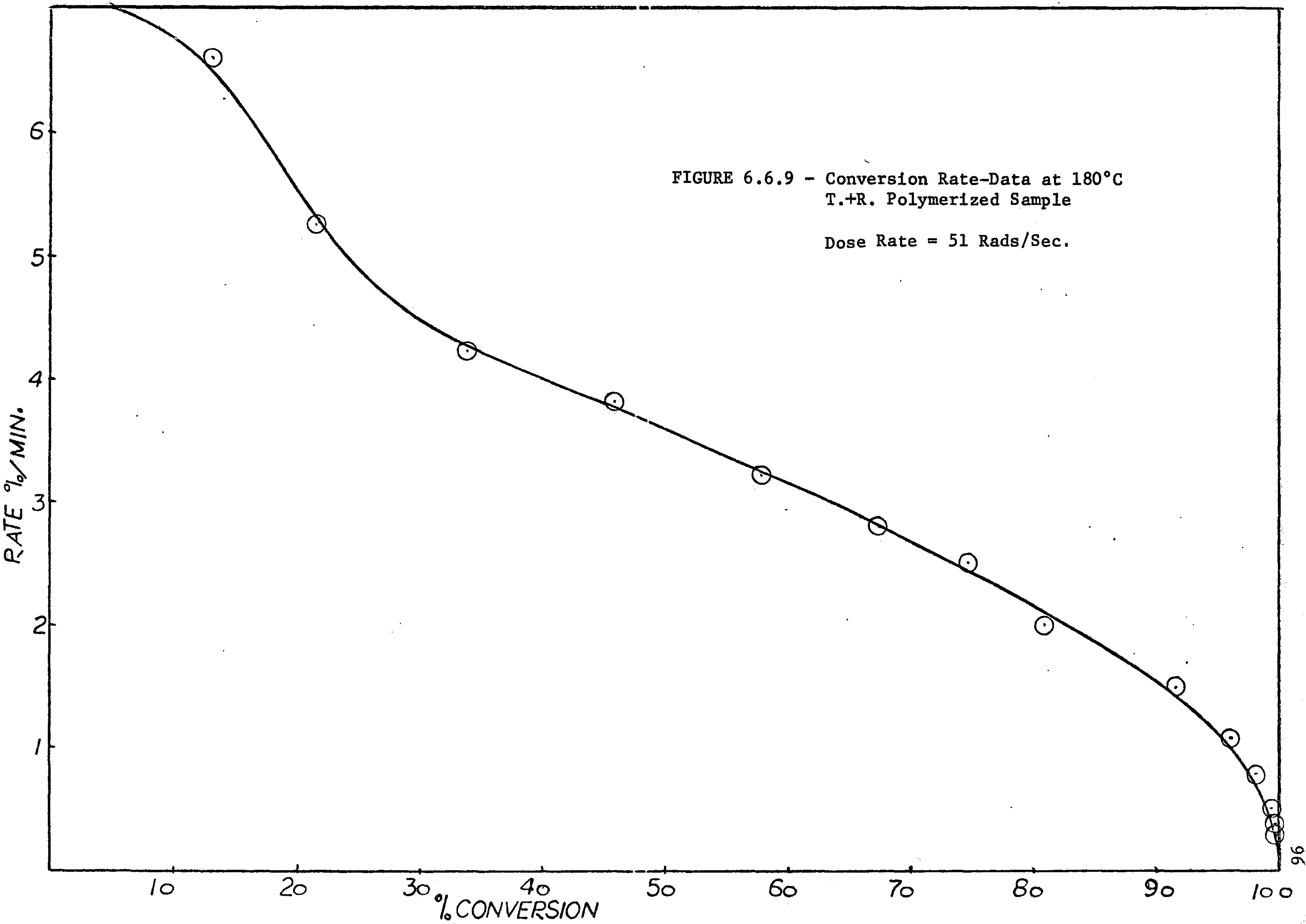


FIGURE 6.6.9 - Conversion Rate-Data at 180°C
T.+R. Polymerized Sample

Dose Rate = 51 Rads/Sec.

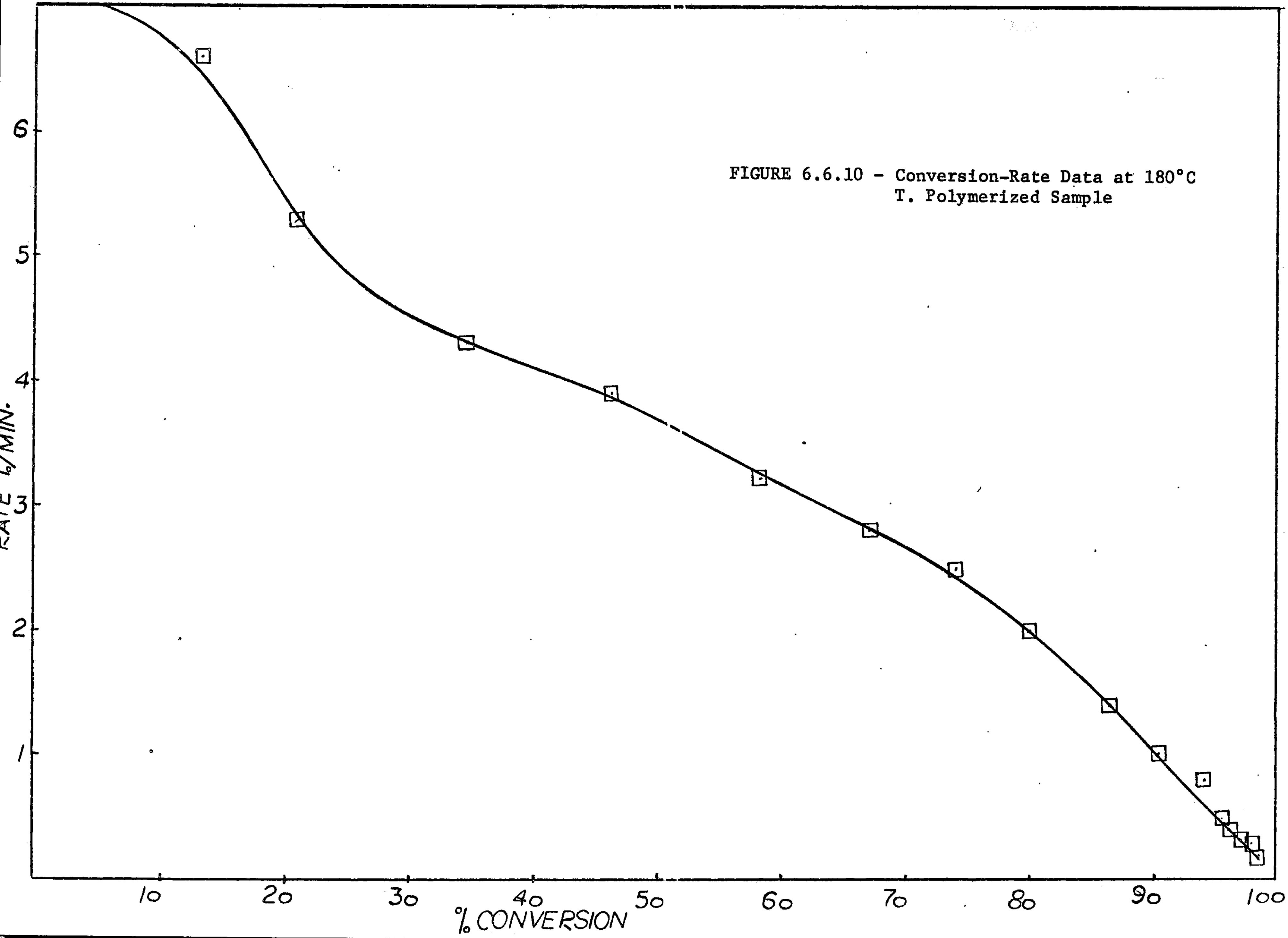


FIGURE 6.6.10 - Conversion-Rate Data at 180°C
T. Polymerized Sample

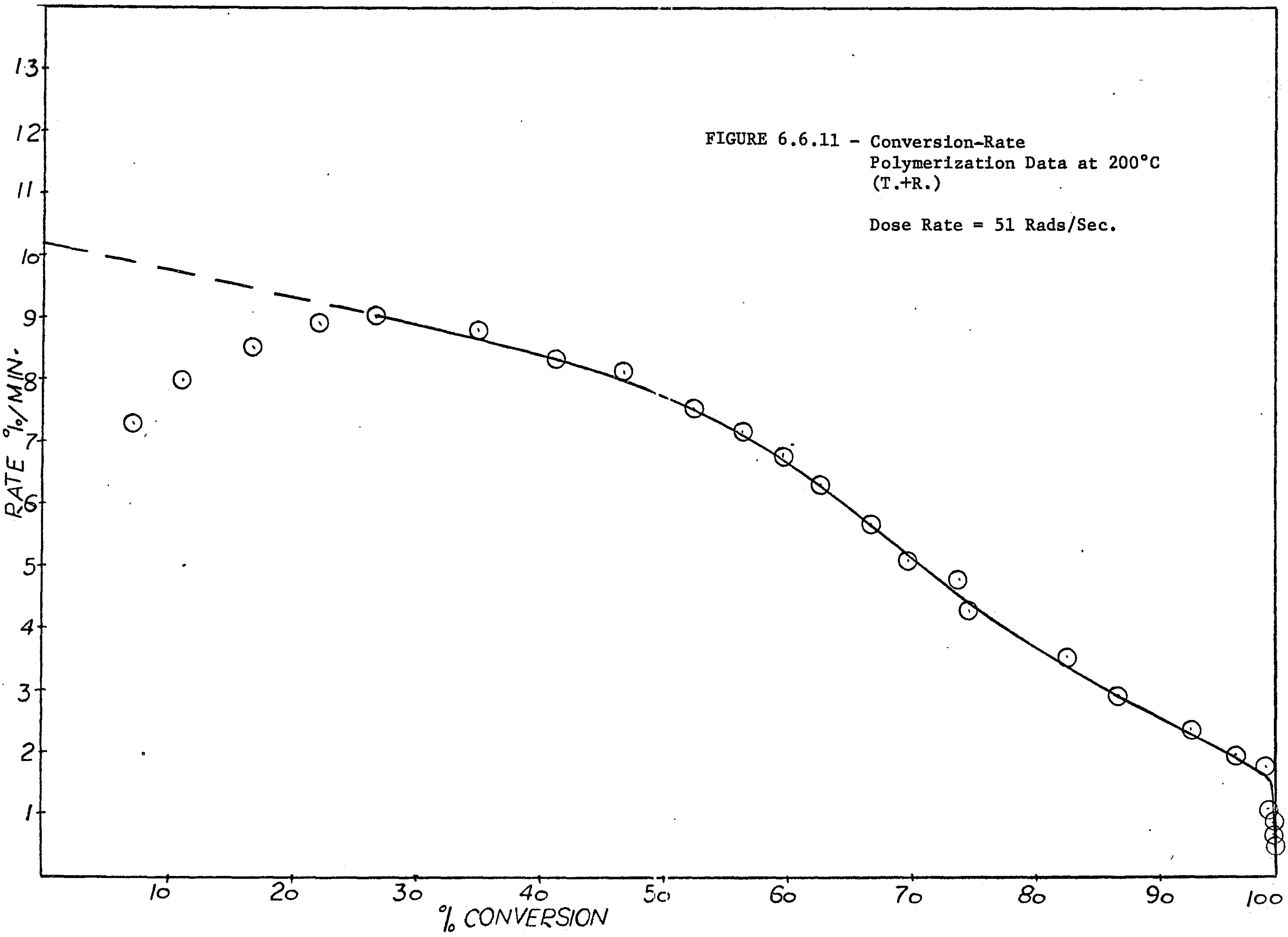


FIGURE 6.6.11 - Conversion-Rate Polymerization Data at 200°C (T.+R.)

Dose Rate = 51 Rads/Sec.

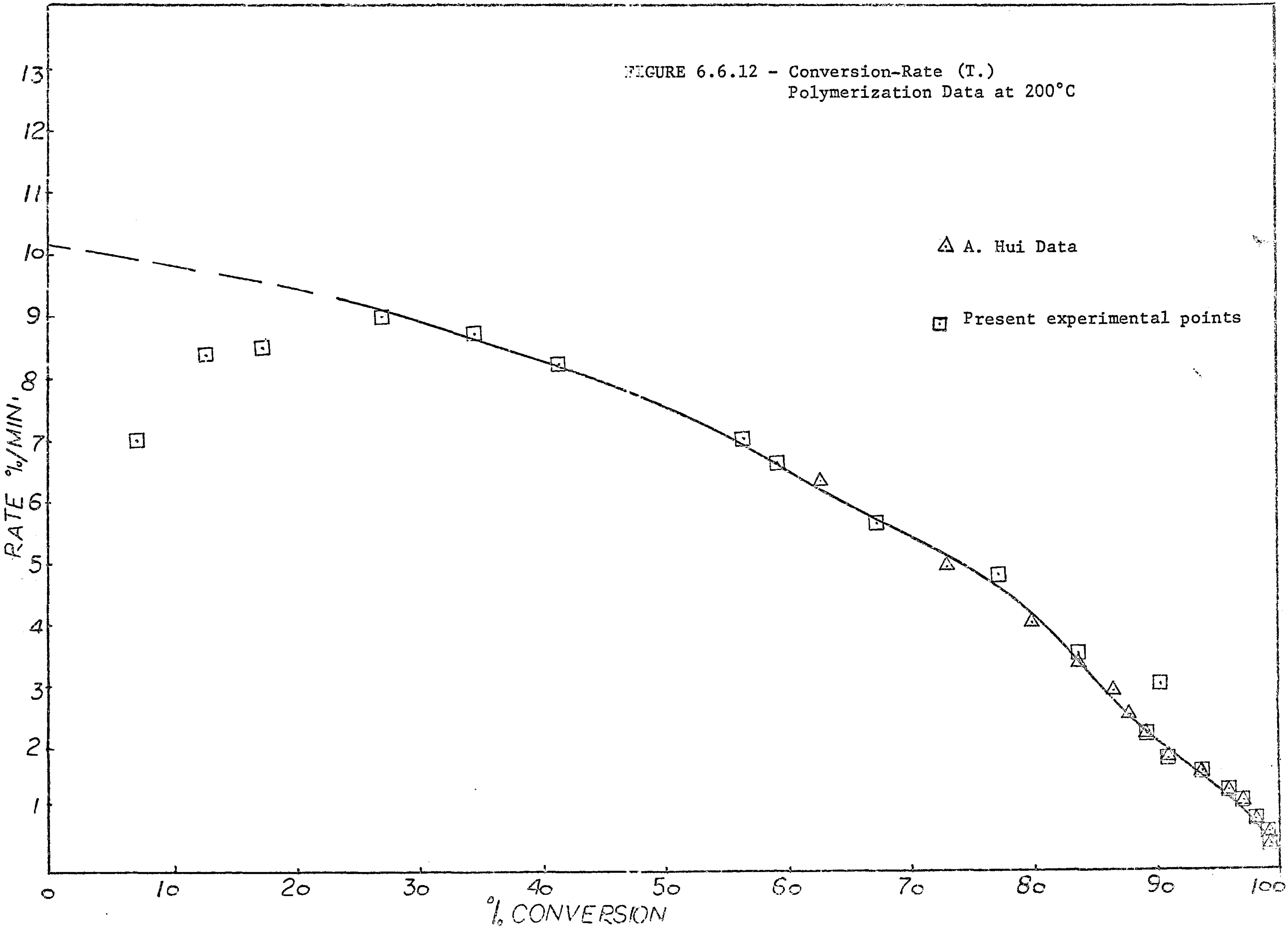


FIGURE 6.6.12 - Conversion-Rate (T.)
Polymerization Data at 200°C

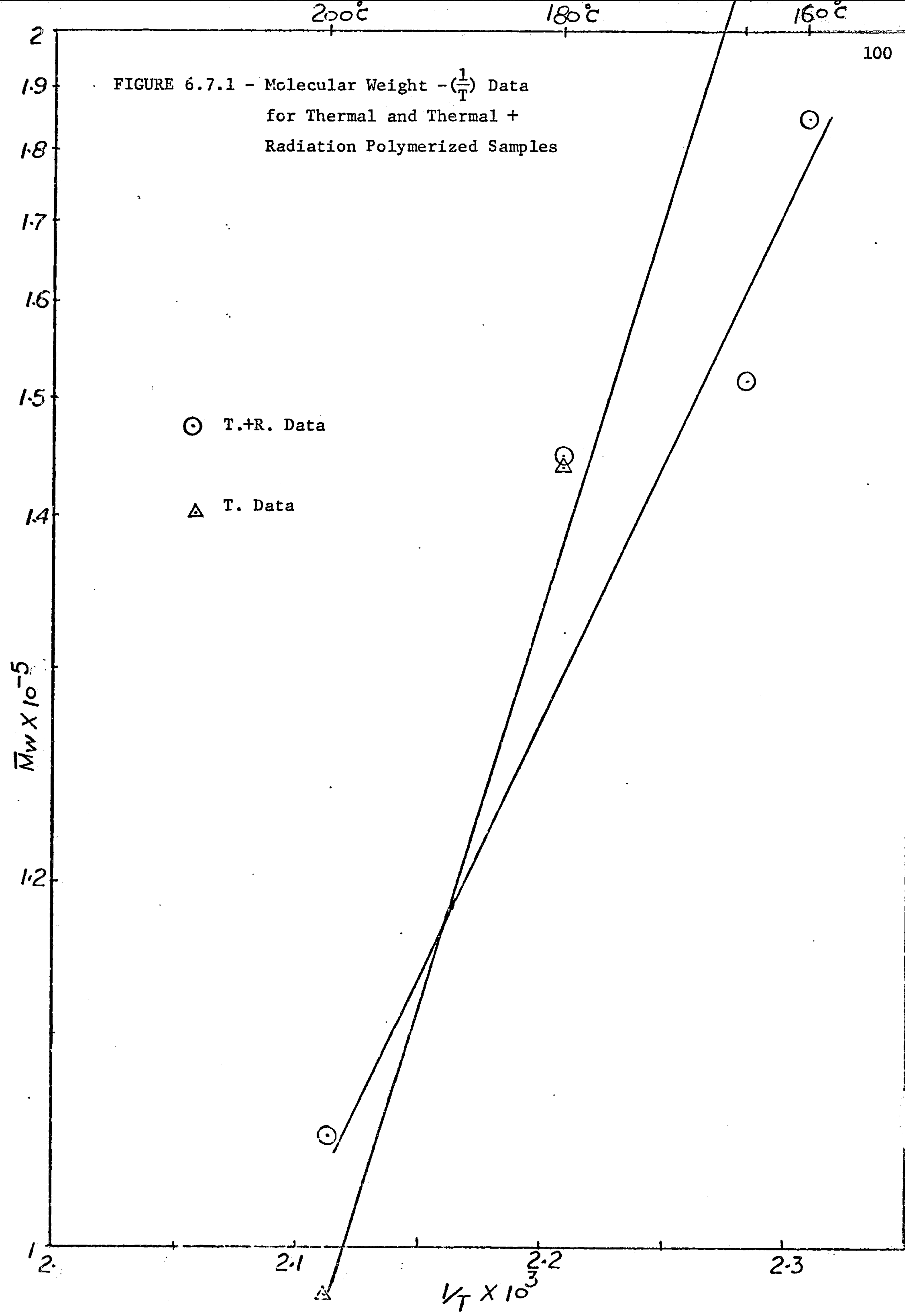


FIGURE 6.7.1 - Molecular Weight -($\frac{1}{T}$) Data for Thermal and Thermal + Radiation Polymerized Samples

(semi-logarithmic plots of molecular weight against reciprocal absolute temperature). The results of G.P.C. analysis are not corrected for imperfect resolution (i.e., infinite resolution).

CHAPTER 7

DISCUSSION OF THE RESULTS

7.1 Dose Rate Independency of Rate of Polymerization

The regressed data giving percent conversion as a function of time showed that the rate of polymerization (%/Min.) was not affected by the dose rate in the temperature range of 150 to 200°C and dose rates of 0.1836 M Rads/hour and 0.072 M Rads/hour. The data points were paired for the two different dose rates and tested to determine if the differences between them were significant. The 't' test with null hypothesis of $\mu = 0$ was used for the analysis. This test will determine whether there is a significant difference between the two sets of data under test in terms of the measurement involved (i.e., whether the mean difference is significantly different from zero). The results show the hypothesis that the mean of the differences is equal to zero is rejected at the confidence level of 98% but can be accepted at the 99% level. For more details about the 't' test the reader is referred to (6).

Therefore, if the confidence limit on the plotted data are expanded to the 99% level, the rate of polymerization can be considered independent of the dose rate.

Chapiro (4) has noticed that the square-root relationship held down to the lowest dose rate investigated, but that at the higher dose rates the exponent decreased slightly below $\frac{1}{2}$, also the degree of polymerization of the polymer showed a similar deviation from the inverse square-root relationship. To explain this phenomenon Chapiro suggests that a portion of the free radicals produced are recombining with each other without initiating polymer chains, thus a limiting free radical concentration must exist. Some other evidence gathered by Chapiro would suggest that this limiting free radical concentration is temperature dependent and that at higher temperatures more free radicals would propagate polymer chains than at lower temperatures. However, the temperature dependence is more complicated at very high dose rates when the various reactions involving primary free radicals compete.

Sood et al (16) has investigated the temperature effects in gamma-initiated polymerization of styrene. His studies were conducted in the temperature range of 50 to 109°C and at dose rates from 0.09 - 0.64 M Rads/hour. In the range of 50-74°C his data agree with the literature, but above 74°C he found that the dose rate exponent decreased as a linear function of temperature, becoming zero at 109°C. In other words, he has found that at 109°C the rate of polymerization, $\bar{R}_p$, and the degree of polymerization $\bar{P}_n$ are independent of the dose rate. It was also predicted that this independency of $\bar{R}_p$ and $\bar{P}_n$ would hold at higher temperatures and at radiation intensity as high as twenty-fold for those studied. For more information about the proposed mechanism of this phenomenon the reader is referred to (16).

Horak et al have done a series of experiments in the temperature range of 119 to 140°C, and at dose rates of 0.1863 to 0.072 M Rads/hour. The results are shown in Table 7.1.1 (63).

His data showed that the prediction of Sood et al was correct and it is to be expected that the rate of polymerization of styrene is independent of the dose rate above 109°C. In the present study this same trend was apparent up to 200°C.

7.2 The Contribution of Radiation to Rate of Polymerization at High Temperatures

A comprehensive study of the polymerization of liquid styrene was conducted by two means; thermally, and by thermal plus radiation, with the objective of investigating the contribution of radiation to the rate of polymerization of styrene at high temperatures.

The experiments were carried on at temperatures in the range of 150 to 200°C and at two dose rates of 0.1836 and 0.072 M Rads/hour. In almost all cases the reactions were studied up to 100% conversion. The conversion time data are reported in Tables 6.3.1 to 6.3.4 (thermal data) and in 6.4.1 to 6.4.10, also Figures 6.6.1 to 6.6.4 show conversion versus time data. The results show that the initial rate of (radiation + thermal) polymerization is rising with temperature in the range 150 to 165°C and is higher than the initial rate of thermal polymerization alone obtained in this investigation and reported in literature (67). At 165°C it becomes evident that both of these

TABLE 7.1.1

Initial Rate of Reaction %/Min. Reported by Horak

Temperature °C	Average Initial T.+R. Rate %/Min. 51 Rads/Sec.	Average Initial T.+R. Rate %/Min. 20 Rads/Sec.	No. of Points Used
119°	0.25	0.24	9
125°	0.42	0.42	7
130°	0.66	0.65	7
140°	0.87	0.87	6

initial rates (rates of radiation + thermal and rate of thermal polymerization) are equal and this was evident at 180°C and 200°C. Each pair of data points were tested satistically (by the 't test' method with null hypothesis of $\mu = 0$) in order to see if the differences between them are significantly different from zero, the hypothesis of $\mu = 0$ is rejected at 98% confidence level but accepted at the 99% level. This test was conducted for conversion up to about 75%.

After about 75% conversion as it can be observed from the Figures 6.6.1 to 6.6.4, the rate of (radiation + thermal) polymerization is noticeably higher than the rate of thermal polymerization. This effect is more pronounced at very high conversions of >95%. In other words, the residual styrene monomer left at conversions above 95% is converted at a much higher rate than in the case of thermal polymerization. This last few percent of monomer has a great bearing on the finished polystyrene products. These effects are discussed in details by Rubens and Boyer (67) and also has already been mentioned in other parts of this report. Figures 6.6.5 to 6.6.12 are conversion versus rate in %/Min. for both experimental conditions, radiation + thermal and thermal polymerization. It is evident from these curves that the rate of polymerization is decreasing as the conversion increases. The same curves have been illustrated in (67, P.218 & 219) for lower temperatures. It is shown that the rate of thermal polymerization is decreasing from the start at 140°C but at lower temperatures the rate remains constant for some period and then decreases. Figures 6.6.5, 6.6.7, 6.6.9 and 6.6.11 show that the rate of (radiation + thermal) polymerization at conversions above 95% are approaching 100% conversion much faster than the thermal rate at the same temperature, or the consumption of monomer at high conversions can be accelerated by the use of radiation. It is also reported by Melville et al (27), that the rate of polymerization decreases rather suddenly after about 2% conversion, although the rate gradually declines throughout the reaction. The essential difference between these curves is the initial increase in rate up to 30% conversion at 200°C thermally or (radiation + thermal). This unexpected phenomena has not been previously reported and apparently does not occur at other temperatures. This effect is probably due to the presence of some retarders which are produced in the system under the conditions of the experiment. Another feature of the results which can be related to the contribution of radiation at high temperature polymerization is the shape of the polymerization rate curves. As can be seen from Figures 6.6.1 to 6.6.4 they exhibit two distinct phases.

It has been reported (14, 15, 16, 43, 44) that polymerization rate curves in the case of radiation are usually 'Sigmoidal' or in other words, they have three distinct regions. The present curves show:

1) A period of relatively rapid polymerization which persists almost to the end of the reaction and for which the rate is exponentially temperature dependent.

2) A final slowing down in rate as the reaction approaches completion and the monomer becomes exhausted. This effect is particularly apparent at lower temperatures.

Because of the lack of data in the literature for high temperature radiation polymerization of styrene, it is not possible at this time to discuss completely the reasons for the above events.

For the case of (radiation + thermal) polymerization of styrene in the range of temperatures below 150°C and above 109°C the only available data are reported by Horak (63). These data are shown in Table 7.1.1. From these data and the present data at 150, 155, 160°C (Table 6.5.1) it is evident that the thermal contribution is increasing with temperature rise above 109°C. The effects of temperature rise are more pronounced at temperatures above 150°C, and the rate of thermal polymerization alone is so significant that the contribution of gamma radiation is negligible. This situation is the reverse of the situation at lower temperatures where the contribution of thermal polymerization can be neglected. Probably there is a temperature between 109°C and 120°C at which these two contributions (gamma and thermal) are approximately equal.

Kinetically it seems feasible to assume that as the temperature rises more and more free radicals are produced by both sources of energy (gamma and thermal) until eventually the population of free radicals becomes so great that they do not initiate chains. This situation is similar to the case which CHAPIRO has predicted (55). His high rates of initiation are accomplished by the combination of high temperature and high dose rate. Probably this is the limiting value for the rate of polymerization. It can be expected that in this system most of the growing chains are terminated by primary free radicals; or in other words, mutual termination by combination or disproportionation does not occur to any appreciable extent. Another point which supports this supposition is that when the stationary concentration of primary free radicals becomes very large in a system the molecular weight of the polymer formed will be low. This is because in this system one can no longer assume that the overall reaction rate is equal to the rate of chain propagation since the rate of monomer consumption through the following step

$$R^{\bullet} + M \rightarrow RM^{\bullet}$$

is becoming appreciable.

Above 165°C one might assume the same situation so that probably the presence or absence of a radiation source does not result in an increase in the rate of polymerization at lower conversions. No attempts were made to measure the rate of initiation at 165°C and higher temperatures to confirm that the initiation step at this temperature and higher is dependent upon temperature alone. A plot of 1/T versus $\ln R_p$ (initial rate of polymerization in %/Min.) is further evidence for this change of mechanism. As can be seen in Figure 7.2.1, the slope of the line is changing at 165°C and becoming smaller in the temperature range of 165 to 200°C. As was mentioned earlier, the rate of destruction of residual styrene monomer at conversions above 95% in the case of (radiation + thermal) polymerization was higher than the thermal rate alone. A justifiable explanation is that, at high conversions when the system becomes viscous only penetrating radiation can be transferred through the polystyrene to reach the trapped monomer and excite the monomer. These free radicals either attack the polymer chains and cause scission or might cause some crosslinking or possibly combine with an inactive polymeric radical. Also, production of polymeric free radicals will consume some of its neighbour monomers.

The fine details of Figures 6.6.5 to 6.6.12 which relate to the exact manner in which rate drops off with increasing conversion should not be taken too seriously, except perhaps in the case of 200°C. The initial rate of polymerization at 200°C should presumably be about 10%/Min. but as the data shows in Tables 6.3.4, 6.4.9 and 6.4.10, the initial rate first increases with conversion and then decreases. It is reported in (51) and it has also been discussed in section 6.5 where it is suggested that the amount of phenyl acethylene or ethynylbenzene produced in styrene at 200°C is enough to function as a retarder for a short time. This substance has been used in industry as a good inhibitor (46). No attempts were made to measure the quantity of this substance.

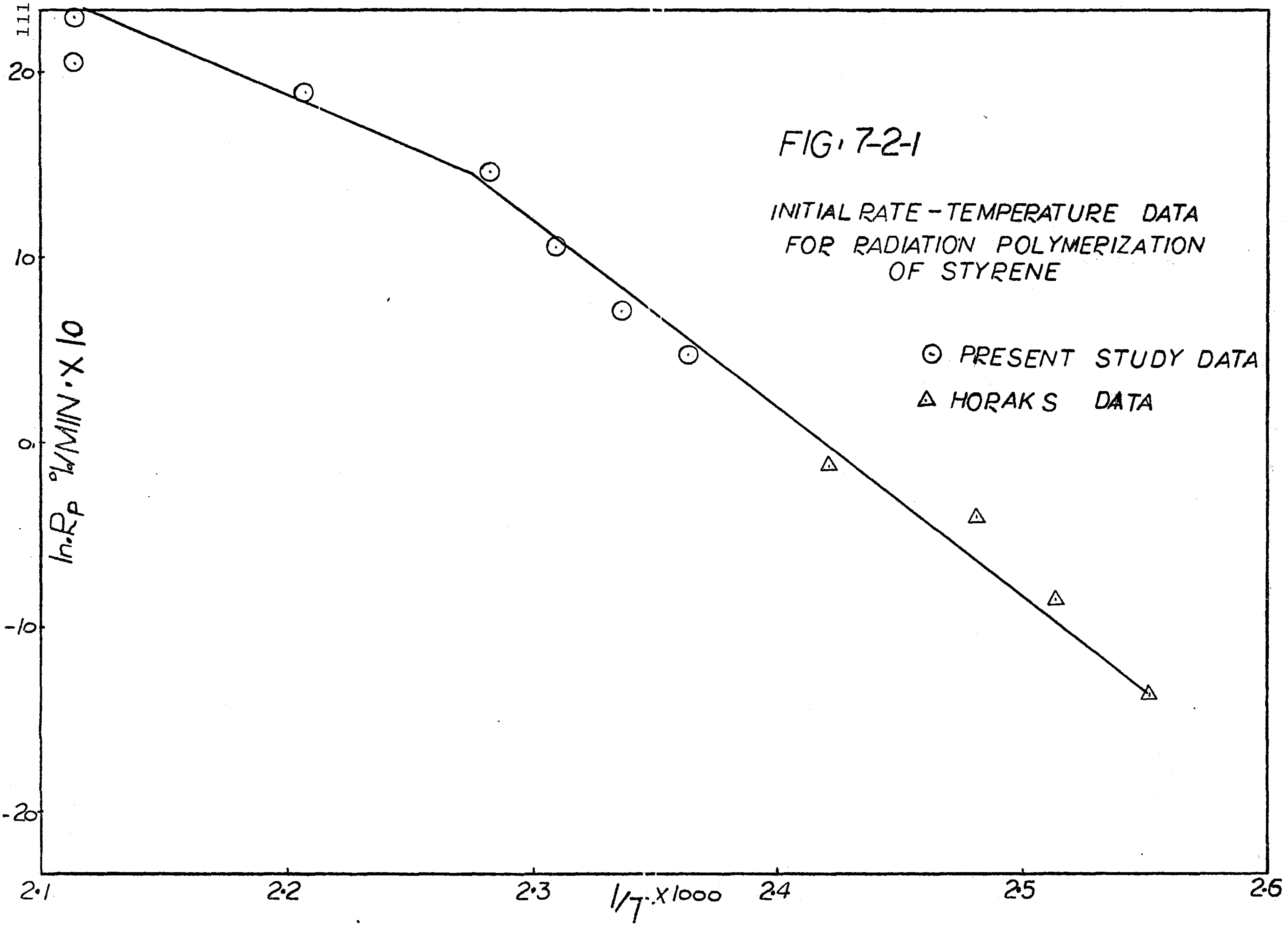


FIG. 7-2-1

INITIAL RATE - TEMPERATURE DATA FOR RADIATION POLYMERIZATION OF STYRENE

For an explanation of the last features of conversion time data which shows 2 distinct phases instead of 3, it is evident from the curves that the rate of polymerization is very high at the start. This rate of polymerization is nearly equal to the rate in the gel effect region during the radiation polymerization of styrene at much lower temperatures (109°C and lower). This effect should not be considered as a gel effect or Trammsdorff effect, however, because the viscosity of the medium is presumably not very high at these temperatures (165 to 200°C) so the termination rate is probably not diffusion controlled. As Hui (18) reported, the gel effect is moderate and less significant with high temperatures and more significant towards low temperatures of say 100°C.

7.3 Physical Nature of Polystyrene Produced

Weight average and number average molecular weights of the (radiation + thermal) and thermal polymerized samples were determined. These results are shown in Table B.4.1 (Appendix B). The samples tested were chosen deliberately at equal conversions from both thermal and (radiation + thermal) polymerized specimens, in order to facilitate comparison. Two types of G.P.C. column packing were used in obtaining the results so that the results would not be expected to be the same. The results of $\bar{M}_w$ and $\bar{M}_n$ determinations at high temperatures (180°C and 200°C) obtained from thermal and (radiation + thermal) polymerized samples were not significantly different.

Any differences which occurred were within the range of experimental error and accuracy of the G.P.C. equipment.

The data at 200°C were in good agreement with the results reported by Hui (18). At lower temperatures (160, 165°C) there were slight differences but they were not very significant, especially since some of the data at 160° and 165° were obtained with another type of G.P.C. packing which could easily account for the difference from the one which was used by the author in the present study. No importance should be placed on these negligible differences. The trend in $\bar{M}_W$ and $\bar{M}_n$ obtained at high temperature is evident. It was clear that the molecular weights of polymer produced by radiation were too low to be of industrial interest.

Chapiro (55) has predicted that in a system with high rates of initiation, some low molecular weight material can be expected because of primary free radical recombination and termination by primary free radicals.

Presumably the same mechanism was obtained in the present investigation as at high temperatures and high intensity of radiation high rates of initiation would result in the system. However, other factors due to the increasing contribution of thermal effect on radiation polymerization should be considered. Some of these factors might be depropagation at high temperatures, chain scission by residual styrene monomer, re-equilibration of the high molecular weight species and degradation thermally or by radiation (11, 18, 61, 67).

The low molecular weight polymers produced by radiation do not prove the generally accepted idea that increased temperatures in radiation polymerization of styrene will be accompanied by production of higher molecular weight polymers (16, 44, 55). There was no apparent evidence in the literature about how significant an increase in molecular weight might be expected and up to what temperature this rise of molecular weight would contine. One would expect a temperature at which molecular weight would start to decrease with further increase in temperature. Apparently the molecular weight of the polymer decreases when the rate of polymerization increases. This was evident from Table B.4.1 (Appendix B) and Table 6.5.1.

Further investigations should be carried out in order to find the difference between the molecular weight of thermal and (radiation + thermal) polymerized styrene if any, and secondly determine the effect of high conversion on the polymers produced by radiation at high temperatures. A third search should be conducted for the critical temperature above which an increase in reaction temperature will decrease the molecular weight. No attempt was made in the present investigation to measure any other physical properties of the polystyrene produced.

7.4 Optimum Temperature for Radiation Polymerization of Styrene

The results thus far have not established the possibility of predicting the optimum temperature for radiation polymerization of styrene.

One of the most important factors which should be considered in the establishment of this optimum temperature is physical property of the polystyrene produced. The two major concerns of industry regarding physical properties of polystyrene are residual monomer in product polystyrene and the average molecular weight. It has already been demonstrated in this investigation that the first goal of elimination of the residual monomer would be achieved at all of the temperatures investigated as polymerization proceeded to 100% conversion in a relatively short time. But, unfortunately the second goal was not accomplished and a very low molecular weight polymer was obtained. It is reported by previous workers (16) that 100% conversion can be achieved at even lower temperatures.

Based on the above consideration and some which have been discussed earlier, it would be worth while to search for the optimum temperature far below 165°C, probably in the range of 110°C to 120°C. There was some consideration given to these two temperatures. 110°C was chosen as the lower limiting value because one wishes to take advantage of the most important facet of radiation polymerization about 109°C (16)---the dose rate independency of the rate of polymerization of styrene. The second temperature limit was set by the consideration that as the reaction temperature increased, the thermal contribution became more and more significant in the rate of polymerization of styrene. This was apparent from data presented in Tables 6.5.1 and 7.1.1 (63).

This influence of the thermal effect on the rate of (radiation + thermal) polymerization probably tends to show more signs of thermal polymerization than radiation polymerization and as it was generally accepted in thermal polymerization any increase in temperature would lower the molecular weight of the polymer (42). By comparison of thermal and (radiation + thermal) rates of polymerization at temperatures well below 165°C it was obvious that there is a temperature not far from 110°C where the contributions of radiation and heat are of equal importance in the rate of polymerization. This temperature may well be the optimum temperature.

Further support for this proposed optimum temperature limit was given by the data of Sood et al (16) which shows high molecular weight polymer produced at 109°C.

7.5 Proposed General Mechanism

It does not appear possible at this time to speak too dogmatically about any of the various reaction mechanisms to be discussed in the following pages, even though one can be reasonably certain of the general correctness of the ideas. It has been generally accepted that the radiation polymerization of styrene is a chain reaction proceeding through a free radical mechanism (14, 15, 16, 32, 43, 55, 65). Some good evidence of this reaction is reported by Chapiro (55).

Kagiya (19) has categorized radiation polymerization and thermal polymerization in the homogeneous liquid state as reactions with slow initiation or stationary polymerization.

Lee (7) has compared the stationary state and non-stationary state thermal polymerization of styrene and concluded that the steady-state condition can be employed for convenience, in kinetic calculations up to high conversions. Hui (18) has reported the same situation for styrene polymerization. Based on Chapiro's (55) proposal, the complete kinetic scheme for high rates of initiation can be written as follows:

(a) Initiation :	RATES
$M \rightsquigarrow 2R^\bullet$	$R_i = \phi_M I[M]$
(b) Recombination of primary radicals:	
$R^\bullet + R^\bullet \rightarrow R_2$	$K_{oo}[R^\bullet]^2$
(c) Addition to monomer:	
$R^\bullet + M \rightarrow RM^\bullet$	$K_{po}[R^\bullet][M]$
(d) Propagation:	
$R^\bullet M_n + M \rightarrow RM^\bullet_{n+1}$	$K_p[RM^\bullet][M]$
(e) Mutual termination:	
$RM^\bullet_n + RM^\bullet_m \rightarrow P_{m+n}$ or $(P_m + P_n)$	$K_t[RM^\bullet]^2$
(f) Termination by primary radicals:	
$RM^\bullet + R^\bullet \rightarrow P_n$	$K_{to}[RM^\bullet][R^\bullet]$

K_t, K_{to} and K_{oo} all pertain to mutual interaction of two free radicals. Usually the magnitudes of the rate constants are about 10^6 to 10^9

liter mole^{-1} sec^{-1}, and

$$K_{oo} > K_{to} > K_t$$

K_{po} and K_p correspond to the reaction of free radical and a vinyl double bond. The activation energy required for this reaction has been reported in the range of 5-8 K cal/mole (55) and the absolute values of rate constants are in the range of 10 to 10^3 liter mole^{-1} sec^{-1}. The stationary state hypothesis has been assumed in this study so the concentration of free radicals can be written as follows

$$\frac{d[R^\circ]}{dt} = 0$$

$$[R^\circ] = \frac{K_{po}[M] + K_{to}[RM^\circ]}{2K_{oo}} \left[\left\{1 + \frac{4K_{oo} R_i}{(K_{po}[M]+K_{to}[RM^\circ]^2)}\right\}^{\frac{1}{2}} - 1\right] \qquad 7.5.1$$

and $$\frac{d[RM^\circ]}{dt} = 0$$

$$[RM^\circ] = \frac{K_{to}[R^\circ]}{2K_t} \left[\left(1 + \frac{4K_{po} K_t[M]}{K_{to}^2[R^\circ]}\right)^{\frac{1}{2}} - 1\right] \qquad 7.5.2$$

These two equations can be simplified for limiting cases of high rates of initiation caused by high dose rate and high temperature:

<u>Situation (1)</u>

If $$R_i >> K_{po}^2[M]^2/4\,K_{oo} \qquad 7.5.3$$

then $$[R^\circ] = R_i^{1/2}/K_{oo}^{1/2} \qquad 7.5.4$$

and $$[RM^\circ] = K_{po}[M]/K_{to} \qquad 7.5.5$$

The overall rate of reaction becomes

$$R_p = K_p K_{po}[M]^2/K_{to} \qquad 7.5.6$$

This equation shows that for very high rates of initiation, the polymerization rate reaches a limiting value where the rate does not increase further when the rate of initiation rises. This situation corresponds to a system in which all growing chains are terminated by primary radicals, i.e. in which reaction (e) does not occur to any appreciable extent. It should be noted that this situation only arises if the stationary concentration of radicals [R°] was very large. It follows that the molecular weight of the polymer formed in such a system was necessarily low. Probably this was the case at 165°C (radiation + thermal polymerization).

Situation (2)

If the average degree of polymerization only corresponds to a small number of monomer units, the rate of polymerization is not equal to the rate of chain propagation since the rate of monomer consumption through step (c) is appreciable. So the rate of monomer conversion is given by

$$R_p = K_{po}[R^\bullet][M] + K_p[RM^\bullet][M] \qquad 7.5.7$$

or

$$R_p = K_{po}[M]^2 \left(\frac{K_p}{K_{to}} + \frac{R_i^{1/2}}{K_{oo}^{1/2}[M]}\right) \qquad 7.5.8$$

If the rate of initiation increases to such an extent that

$$R_i^{1/2} >> K_p\ K_{oo}^{1/2}[M]/K_{to} \qquad 7.5.9$$

Then

$$R_p = K_{po}\ K_{oo}^{-1/2}\ R_i^{1/2}[M] \qquad 7.5.10$$

This equation has the same form as the classical equation

$$R_p = K_p/K_t^{1/2}\ R_i^{1/2}[M]$$

but here K_{po} and K_{oo} appear instead of K_p and K_t respectively. Hence it can be concluded that when this situation arises most of the chains initiated in step (c) are immediately terminated by step (f). The polymer obtained in this situation will have a very low molecular weight, scarcely high enough to justify the term polymer. Situation (2) would be expected for temperatures of 200°C and higher.

The general kinetic mechanism for free radical polymerization of styrene, as described above, was entirely dominated by the following three reaction steps, all involving primary radicals. These reaction steps were proposed by Chapiro.

(b) $R^{\circ} + R^{\circ} \rightarrow R_2$

(c) $R^{\circ} + M \rightarrow RM^{\circ}$

(d) $R^{\circ} + RM_n^{\circ} \rightarrow P_n$

The general features of the overall product were determined to a large extent by the result of their competition. If reaction step (c) was largely dominant, all primary radicals would be used to initiate polymerization. The rate of this reaction can be written as

$$R_{(c)} = K_{po}[R^{\circ}][M]$$

K_{po} is closely related to the propagation step in vinyl polymerization so step (c) should require an energy of activation of the order of 5 to 8 K cal/mole. This was the case in radiation polymerization of styrene at temperatures up to 109°C (16).

The other two reaction steps (f) and (b) involve free radical combination reactions and require a very low activation energy. These two steps probably are involved in the polymerization of styrene at temperatures above 165°C. So, generally for styrene polymerization with radiation an increase in temperature up to presumably 120°C would chiefly favour reaction step (c) in its competition with (b) and (f) (16, 44, 55).

Degree of polymerization for the two situations discussed can be obtained from the following equations:

Situation (1)

$$\bar{P}_n = R/K_{po}[M][R^\bullet] = K_p(K_{oo}{}^{1/2}/K_{to})R_i{}^{-1/2}[M] \qquad 7.5.11$$

Situation (2)

$$\bar{P}_n = [M]\ [\frac{K_p}{K_{to}} \cdot \frac{K_{oo}}{R_i{}^{1/2}} + \frac{1}{[M]}\ ] \qquad 7.5.12$$

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

Radiation induced polymerization and thermal polymerization of styrene saturated with water were conducted in the temperature range 150-200°C and dose rates of 0.072-0.1836 M Rads/hour. Close examination of different stages of reaction has led to the following conclusions.

1) Rate of polymerization was independent of the dose rate in the temperature range 150-200°C confirming the previous investigation by Sood et al and Horak et al (16, 63).

2) As the temperature increases the contribution of the thermal component in the rate of (radiation + thermal) polymerization was more and more significant and eventually at 165°C the initial rate of (radiation + thermal) polymerization becomes equal to the rate of thermal polymerization alone. This equality occurs up to 200°C and presumably at even higher temperatures as well. 165°C was considered to be the temperature at which the radiation polymerization system in the case of styrene reaches a limiting rate of initiation caused by high temperature and dose rate. Above this

temperature the initial rate of radiation polymerization does not increase further when the rate of initiation rises.

3) Above 165°C the initial rate of polymerization of styrene was independent of the radiation source (intensity range of 0.072-0.1836 M Rads/hr), and this independency continued up to about 75% conversion. Above this conversion the contribution of gamma radiation on the rate of polymerization was evident because the rate of (radiation + thermal) polymerization was higher than the rate of (thermal) polymerization. There was a significant difference between the time required to eliminate the residual styrene monomer above 95% conversion by radiation and by thermal. At 165°C the time required to eliminate the last 5% of monomer in a 95% converted polystyrene mixture was only about 2 hours with radiation treatment and 6 hours or more with just thermal.

Although radiation provides a means for destruction of the residual monomer in highly converted polymer, rather it would be industrially advantageous to start radiating much earlier in the polymerization process, affording a considerable reduction in total process time.

4) Self-production of ethynylbenzene (phenyl acethylene) in the system at 200°C probably caused retardation of the initial rate of polymerization of styrene at this temperature.

5) There was no apparently significant Trommsdorff effect (gel effect) in the investigated temperature range.

6) Average molecular weights of these polymer were very low and were decreasing with increase in temperature for both conditions of the experiments. In the case of (Radiation + Thermal) polymerization these results were not in agreement with the generally accepted mechanism of radiation polymerization according to which the higher the temperature, the higher the molecular weights. This contradication was probably due to the high contribution of the thermal component in the (radiation + thermal) polymerization, which most likely caused depolymerization, degradation and chain scission.

7) It is not possible with the present data to determine a specific optimum temperature for the radiation polymerization of styrene. However, from the trends of the data the desired temperature should be in the range of 110-120°C.

8) A general mechanism was proposed, but because of the lack of data at the present time no attempts were made to test the applicability of this mechanism.

8.2 Recommendations

The present investigation indicates that polymers produced by radiation polymerization above 160°C do not have the desired industrial properties. There is a serious lack of data in literature for radiation polymerization of styrene in the range of 110° to 150°C. Considering the independency of the rate of polymerization from dose rate above 110°C probably more investigation is needed to establish an optimum condition for radiation polymerization above this temperature. This investigation should cover the studies of complete conversions (0-100%), physical properties of produced polymer, kinetic mechanism of the reactions, and should eventually result in a model which can predict conversion and molecular weight of the polymer.

The evidence of the present study and the literature imply that there should be a temperature at which the radiation polymerization of styrene will produce a maximum molecular weight polymer and above this temperature the molecular weight will decrease with an increase in temperature. Also, there should be a temperature at which the contribution of the thermal component and radiation component to the rate of (radiation + thermal) polymerization are equal. From the results of the present investigation probably these two temperatures are both in the range of 110 to 120°C so this range should be investigated carefully. Testing of the proposed general mechanism should go far towards prediction of the kinetic model at temperatures above 110°C. A study of the relation between molecular weight and conversion is recommended in radiation polymerization at high temperatures which should lead to the measurement of the amount of degradation or depolymerization of polystyrene at those temperatures.

BIBLIOGRAPHY

1. Chem. and Eng. News 1969 (Monthly Report, July to Dec. 1969).

2. Chem. and Eng. News 1970 (Monthly Report, July to Dec. 1970).

3. Blyth, J. and Hoffman, A.W., Ann. 53, 292-329 (1845).

4. Chapiro, A., "Radiation Chemistry of Polymeric Systems", Interscience, New York-London, Chapter V (1962).

5. Balke, S., Chemical Engineering Dept., McMaster University, Private Communication (1970).

6. Volk, W., "Applied Statistics for Engineer", McGraw-Hill, New York, P.111 (1958).

7. Lee, W.M., J. Polymer Sci., Polymer Letter PT.B. V.6, 603 (1968).

8. Boundy and Boyer, "Styrene - Its Polymers, Copolymers and Derivatives", Reinhold, New York, Chapter 8 (1952).

9. Uneo, K., Williams, F., Hayashi, K. and Okamura, S., Faraday Soc. Trans., V.63, no. 534, 1478 (1967).

10. Boundy and Boyer, "Styrene - Its Polymers, Copolymers and Derivatives", Chapter 10, 11 (1952).

11. IBID. P.609, P. 637.

12. Chem. and Eng. News, June 29, 1970.

13. Modern Plastic, Dec. 1970.

14. Dean, D., "The Radiation Initiated Polymerization of Styrene", Thesis, McMaster University (1968).

15. Elaraby, S.M., "Post Irradiation Study of Highly Converted Styrene and Polystyrene Systems", Thesis, McMaster University (1970).

16. Sood, S.P. and Hodgins, J.W., J.Polymer Sci., Submitted for Publication, Jan. (1971).

17. Ballantine, D.S., Isotopes and Radiation Tech., V.6, N.2, 164 (1969).

18. Hui, A.W.T., "Kinetics of Free Radical Polymerization of Styrene to Complete Conversion", Thesis, McMaster University (1970).

19. Kagia, T., Izu, M. and Fukui, K., Bull. Chem. Soc., Japan, V.40, 1045 (1967).

20. Chapiro, A., "Radiation Chemistry of Polymeric Systems", Interscience, New York-London, Chapter II (1962).

21. Newell, J.E., Anal. Chemistry, V.23, N.3, 445 (1951).

22. Boundy and Boyer, "Styrene - Its Polymers, Copolymers and Derivatives:, Reinhold, New York, Chapter 3 (1952).

23. Chapiro, A., "Radiation Chemistry of Polymeric Systems", Interscience, New York, Chapter VII (1962).

24. IBID, P. 606.

25. Huglin, M.B., Chem. and Process Eng., V.49, N.10, 104 (1968).

26. Charlesby, A., "Atomic Radiation and Polymers", Pergamon Press, New York, Chapter 4 (1960).

27. Melville, H.W., and Valentine, L., Trans. Faraday Soc., V.46, 210 (1950).

28. Charlesby, A., "Atomic Radiation and Polymers", Pergamon Press, New York, Chapter 5 (1960).

29. IBID. Chapter 2 (1960).

30. American Society for Testing Materials, ASTM, D1671-63.

31. Flory, P.J., J.Am.Chem.Soc., 59, 241 (1937).

32. Charlesby, A., "Atomic Radiation and Polymers", Pergamon Press, New York, Chapter 22 (1960).

33. Swallow, A.J., "Radiation Chemistry of Organic Compounds". Pergamon Press, New York, Chapter II, Part A (1960).

34. IBID, Chapter II, Part C (1960).

35. Burton, M., Dis. Faraday Soc., 12, 317 (1952).

36. Eyring, H., Hirschfelder, J.O. and Taylor, H.S., J. Chem. Phys. 4, 479, 570 (1930).

37. Shimomura, T., Smid, J. and Szwarc, M., Am. Chem. Soc., Div. Polymer Chem., V.8, N.2, 897 (1967).

38. Boundy and Boyer, "Styrene - Its Polymers, Copolymers and Derivatives", Reinhold, New York, Chapter 9 (1952).

39. Charlesby, A., "Atomic Radiation and Polymers", Pergamon Press, New York, P.290 (1960).

40. Manowitz, B., Horrigan, R.V. and Bertton, R.H., B.N.L. 141 (T-27) (1951).

41. Ballantine,D.S., Glines, A., Metz, D.J., Beher, J., Mesrobian, R.B. and Restaino, A.J., J. Polymer Sci., 19, 219 (1956).

42. Cohen, S.G., J.Am. Chem.Soc., 67, 17 (1945).

43. Srinivasan, S., Nuclear Science Abstract, V.19, 28362 (1965).

44. Ballantine, D.S., Colombo, P., Glines, A. and Manowitz, B., Chem.Eng. Prog., 50/11, 267 (1954).

45. Tobolsky, A.V., J.Chem.Phys., 12, 402 (1944).

46. U.S. Patent No.2, 241, 770, May 13 (1941).

47. Blachford, J. and Robertson, R.F., J. Polymer Sci., P.A. V.3, 1311 (1965).

48. Hodgins, J.W., Werezak, G.N. and Ross, S.L. Can.J.Chem.Eng., 43, 117 (1965).

49. Kolthoff, I.M. and Dale, W.J., J.Am.Chem.Soc., 69, 441 (1947).

50. Gillham, R,C., Trans. Faraday Soc., 46, 497 (1950).

51. Boundy and Boyer, "Styrene - Its Polymers, Copolymers and Derivatives", Reinhold, New York, Chapter 5 (1952).

52. Duerksen, J.H., "Free Radical Polymerization of Styrene in Continuous Stirred Tank Reactor", Thesis, McMaster University (1968).

53. Moor, J., J.Polymer Sci., A.2, 835 (1964).

54. C.I.C. Meeting Notes, "Polymer Reactors and Molecular Weight Distribution", Niagara Falls (1967).

55. Chapiro, A., "Radiation Chemistry of Polymeric Systems", Interscience, New York-London, Chapter IV (1962).

56. Lewis, F.M. and Mayo, F.R., Ind. Eng. Chem., Anal. Ed., 17, 134 (1945).

57. Eisenbrand, J., and Eich, H.W., Z.Anal.Chem., 175, 4 (1960).

58. Trujillo, E.F., "Model DK-A Ratio Recording Spectrophotometers", Beckman Instruments Inc., California (1962).

59. Fischer, R.B., "Quantitative Chemical Analysis", W.B. Saunders Co., London (1964).

60. Werezak, G.N., "Gamma Induced Chlorination of Methane, Ph.D. Thesis, McMaster University, P.215 (1966).

61. Charlesby, A., "Atomic Radiation and Polymers", Pergamon Press, New York, Chapter 10 (1960).

62. Boundy and Boyer, "Styrene - Its Polymers, Copolymers and Derivatives", Reinhold, New York, Chapter 6 (1952).

63. Horak, Z. and Hodgins, J.W., "Radiation Polymerization, of Styrene at High Temperatures", Unpublished Data, McMaster University (1970).

64. Charlesby, A., "Atomic Radiation and Polymers", Pergamon Press, New York, Chapter 3 (1960).

65. Chen, C.S.H. and Stamm, R.F., J.Polymer Sci., 58, 369 (1962).

66. Chapiro, A., "Radiation Chemistry of Polymeric Systems", Interscience, New York, Chapter I (1962).

67. Boundy and Boyer, "Styrene, Its Polymers, Copolymers and Derivatives", Reinhold, New York, Chapter 7 (1952).

68. Charlesby, A., "Atomic Radiation and Polymers", Pergamon Press, New York, P.467 (1960).

69. Chem. and Eng. News, Dec. 14 (1970).

70. Hopwood, F.L. and Phillips, J.T., Proc. Phys. Soc. (London) 50, 438 (1938).

71. Metz, D.J. and Ballantine, D.S., Polymer Sci., Current Concepts and Civid Applications (Annals of N.Y. Acad. of Sci., V.155, Article 2, Jan. 27, 1969, P.468-81).

APPENDIX A

Experimental Details

A.1 Reactor

A.1.1 Irradiation Source

Associated with the McMaster reactor is a radiation laboratory rated at 10,000 Curies of Cobalt 60. This laboratory is provided with an observation window, manual slave manipulators, an electric hoist, a water tunnel for storage of the source when room entry is necessary and a pass through system communicating with the reactor pool. The source itself has a nominal strength of 5,000 curies of Cobalt 60.

The active materials are kept in the 12 rods of 0.445 inch diameter and $8\frac{15}{16}$ inch overall length. These twelve pencils occupy twelve positioning tubes which are distributed in a cylindrical cage of 7 inches long and 3 inches I.D. A full description of the source is given in reference (48), and Figure A.1.1.

A.1.2 Reaction Vials

All polymerization reactions were carried out in annealed pyrex glass vials.

Bulk polymerization of styrene is an exothermic reaction. In order to have the isothermal condition necessary for kinetic studies, rapid attainment of the temperatures in question is necessary. It is because styrene monomer and polystyrene are poor conductors, 18 MM O.D. vials were of little use in the study, the long heat paths result in slow dissipation of the heat of reaction, (62), also, at

CO-60 PENCIL HOLDER

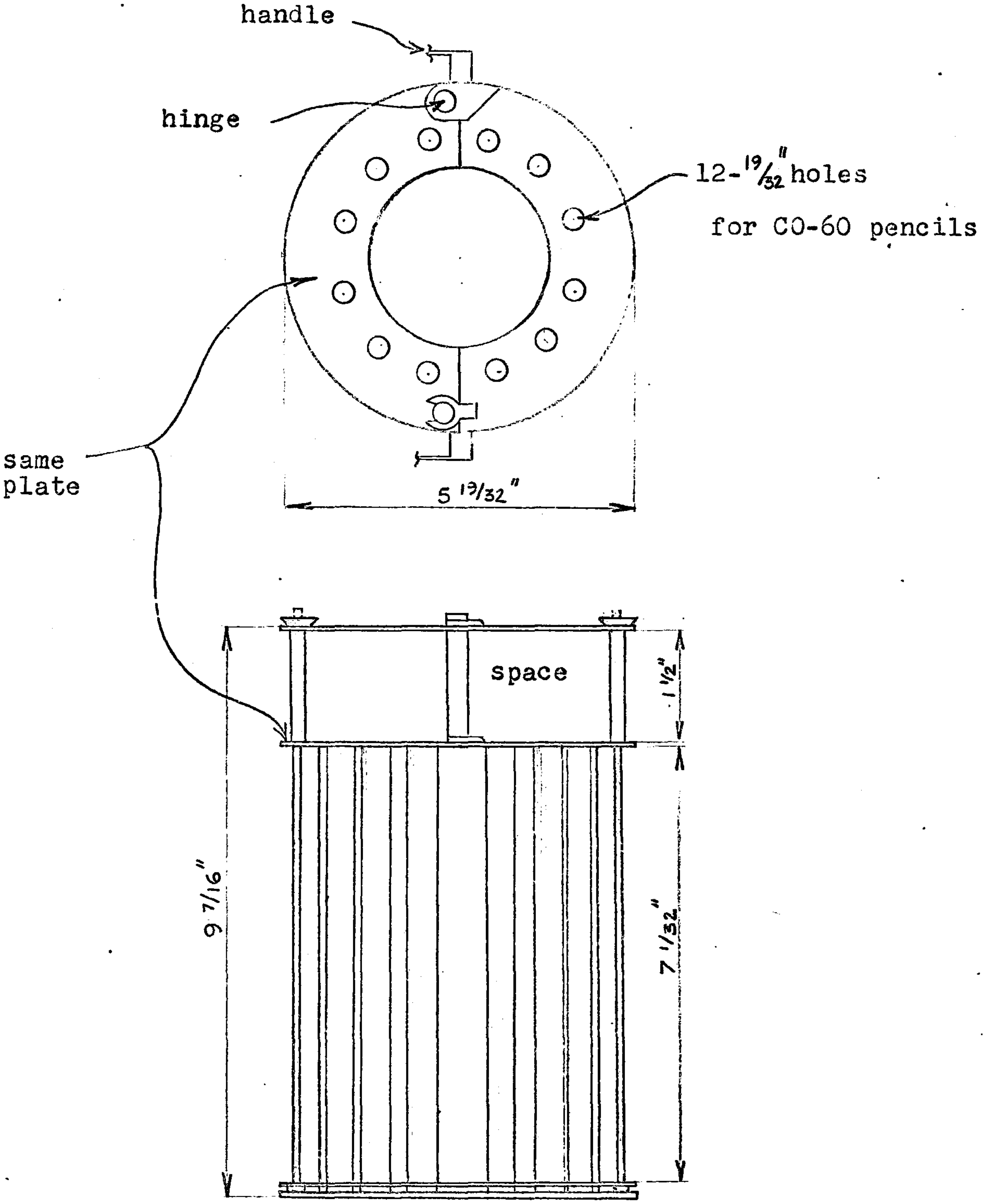


FIGURE A-1-1-1

the start of the reaction the time lag for the styrene in the vial to reach the desired reaction temperature was long enough to introduce significant error, particularly for short irradiation times. A 5 MM O.D. vial was very good from this point of view, but the amount of sample which was obtained was not enough for accurate analysis. Between 7 and 8 MM O.D. the 7 MM was chosen as the one being closest to the optimal conditions. Each of these vials was connected to the vacuum system by means of a standard male B.14 tappered joint. The overall length was $12\frac{1}{4}$ inches. $6\frac{3}{4}$ inches from the bottom of the vial a small flange was provided in order to be held at the proper height in a special glass funnel in the sample holder. The complete geometry of the vials is shown in Figure A.1.2.1.

A.1.3 Irradiation Reactor

The equipment which was used by the previous workers in this group for the investigation of radiation polymerization was a cylindrical sample holder concentric with the γ source contained in an air-bath.

The first set of experiments showed that these facilities were not adequate at the conditions of the present investigation for the following reasons:

1) lack of accurate temperature control,
2) poor heat transfer between the bottom of the air bath and the top. The temperature difference was nearly 50°C and from one cylinder to another about 4-8°C,

VIALS

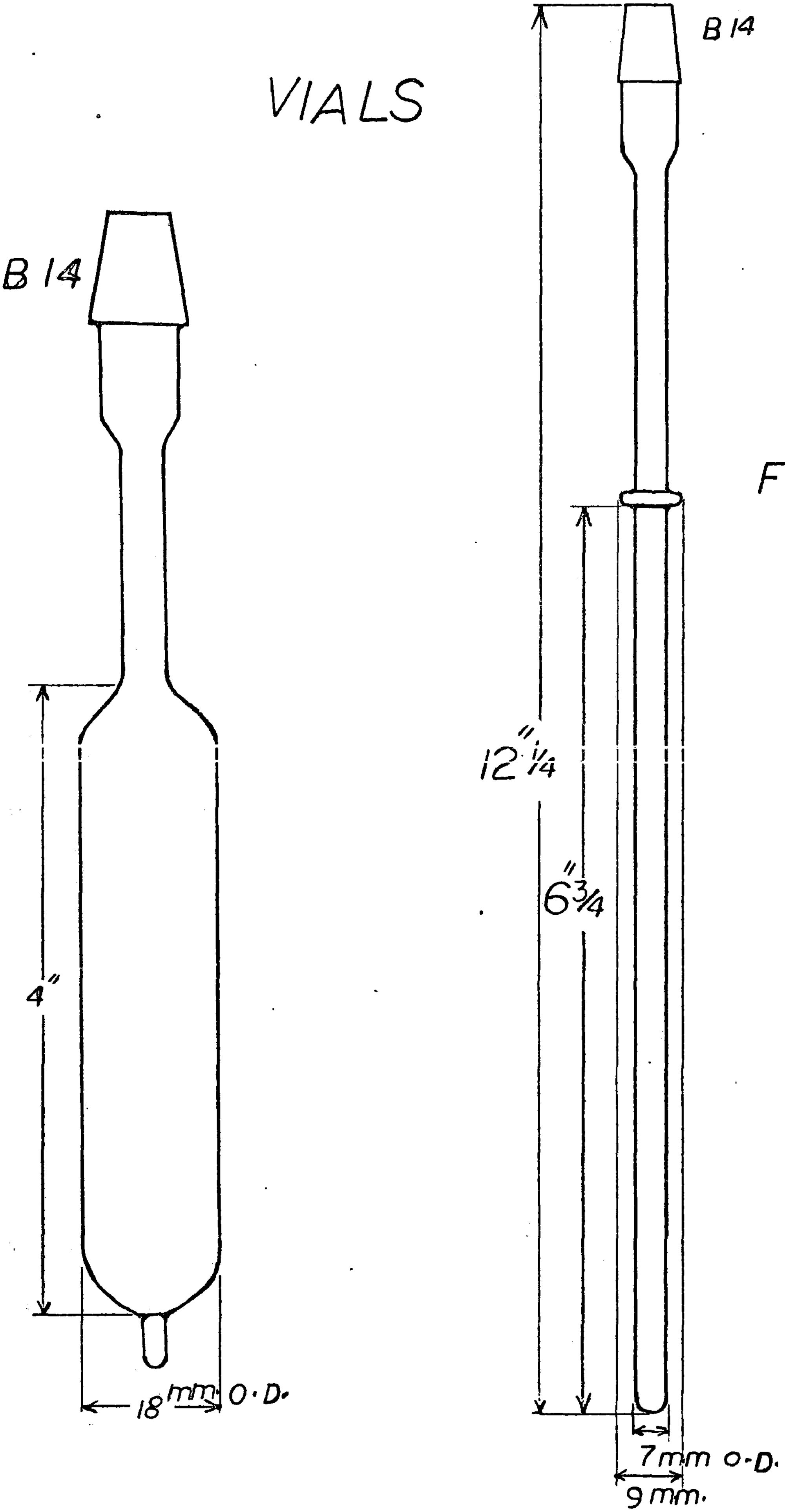


FIG. A-1-2-1

3) difficult manipulation of the samples. It takes about 12 minutes to put the samples in the bath and during this time and the time of source manipulation one can have a large error due to thermal polymerization (for example, the thermal conversion of styrene at 200°C after 12 minutes is about 68%).
4) low heat transfer coefficient at the air-sample interface.

For these reasons a BLUE-M constant high temperature oil bath was obtained. It was equipped with a magnetic agitation system and a highly sensitive temperature control.

A specific type of oil (23 imperial gallons) is used in this oil bath because of the effects of gamma radiation on hydrocarbon oils. This oil, 'Terphenyl' is the organic coolant used in the Whiteshell Nuclear Reactor. According to the McMaster atomic reactor regulations, there should not be an emission of vapour because it can condense around the rubber gaskets of the building and cause some leakage in the system. The boiling point of terphenyl is 365°C at 760 MM Hg, so it has a suitably low vapour pressure at 200°C (maximum temperature during the investigations), not only is the medium resistent to gamma radiation, but it is not a strong gamma absorber.

A new sample holder was designed consisting of a stainless steel cylinder and 3 circular slots which were welded to the circumference of the cylinder. The cylinder has an inside diameter of $5\frac{13}{16}$ inches which is about $\frac{7}{32}$ inches bigger than the O.D. of the source cage, and a height of $7\frac{7}{8}$ inches. The slots were situated at radial distances of $3\frac{3}{8}$, 4 and 6 inches from the axis of the source. The width of each slot was exactly $\frac{3}{8}$ inches and the number of vials which can be held in each slot was 32, 36 and 56 respectively, proceeding from the axis of the source. In order to hold the vials in these slots a special glass funnel was designed with a long stem and a short head. The advantage of the long stem is that it keeps the vials from moving back and forth which will cause different dose desorption in the samples. The head is a guide in positioning the vials inside the funnels by remote control slave manipulators. The whole assembly was supported by means of 6 stainless steel bars on the shoulder of the oil bath. Complete geometry of the sample holder and the funnels is shown in Figures A.1.3.1, A.1.3.2 and A.1.3.3 respectively.

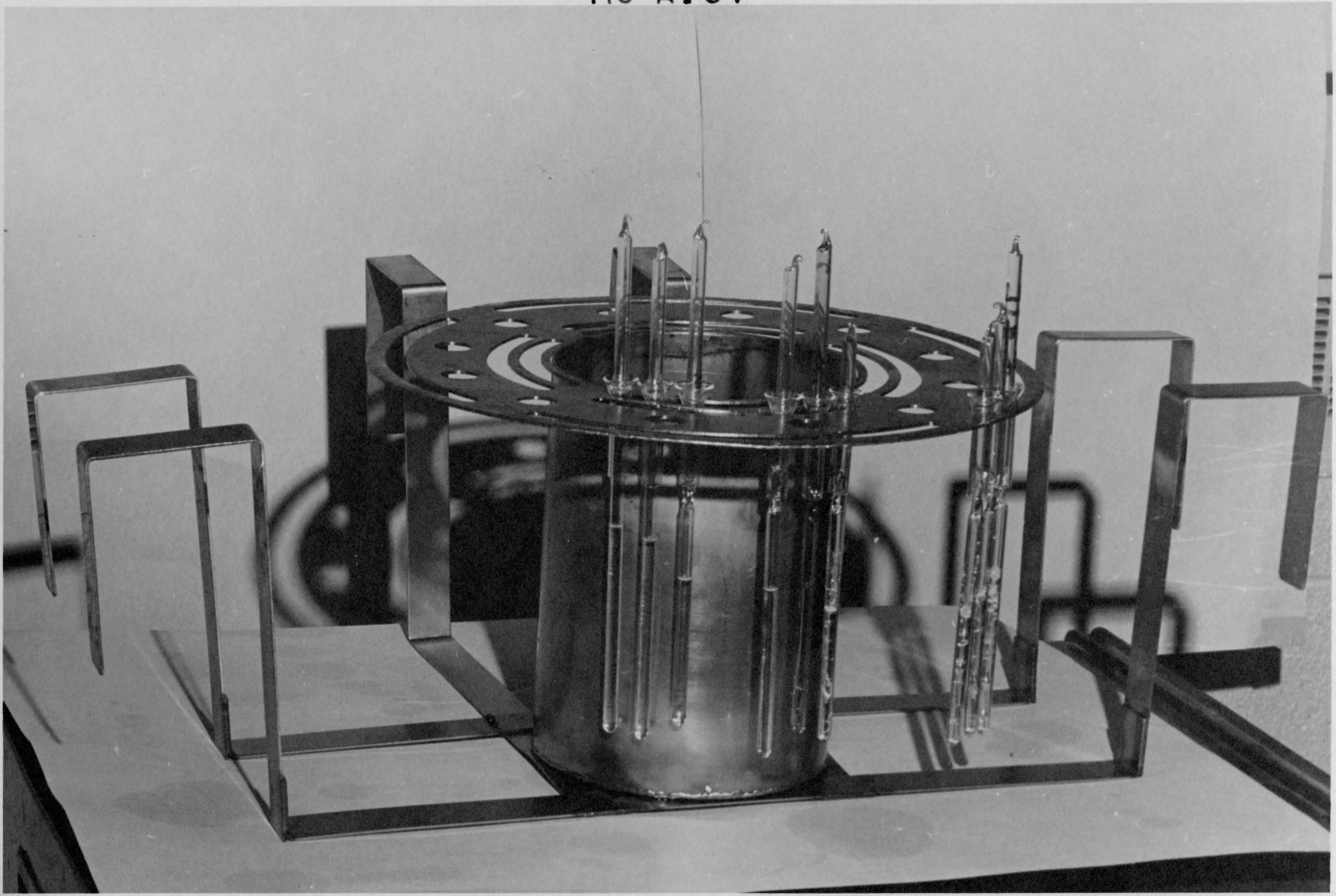
A.2 Sample Preparation

Nearly 300 samples were prepared. The preparation of these samples consists of several steps as shown below.

A.2.1 Cleaning of Reaction Vials

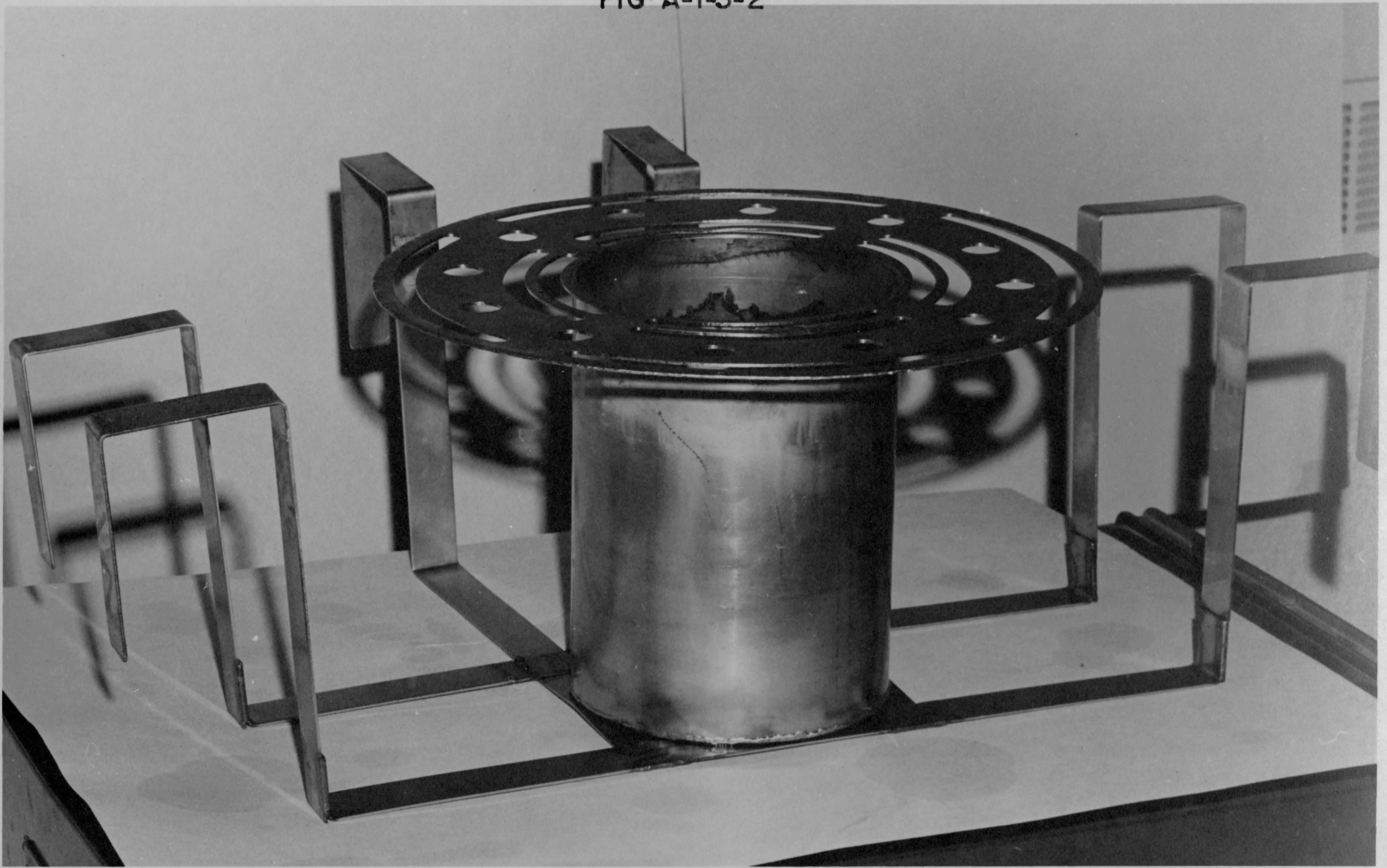
The rate of polymerization is very sensitive to the presence of trace impurities, especially organic materials. In order to have clean vials, they were washed with chromic acid, rinsed 5 times with tap water, 5 times with distilled water and 3 times with acetone, and finally dried at 120°C for 3 to 4 hours in an oven.

FIG. A-1-3-1



SAMPLE HOLDER WITH VIALS

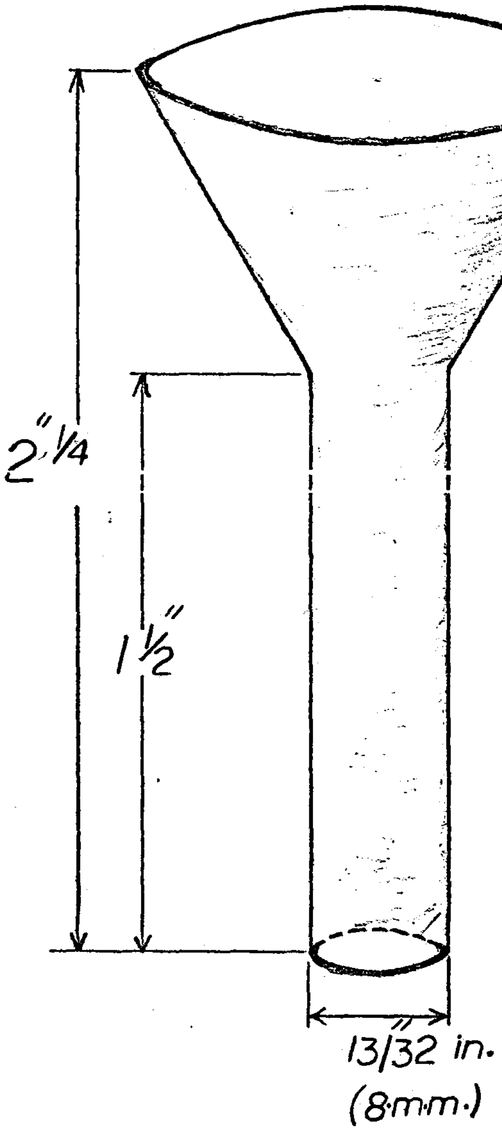
FIG· A-1-3-2



SAMPLE HOLDER

FIG· A-1-3-3

"FUNNEL"



A.2.2 Vacuum Test and Vial Filling

The clean vials were evacuated and tested with a leak detector coil. A 10 cc hypodermic syringe fitted with a 19 gauge, 11.5 inch hard glass needle was used to fill the vials with styrene.

Each vial was filled with about 1.5 cc of styrene; (depth in vial about 3 inches). More details about the necessity of having only 1.5 cc of styrene in the vials will be given in the sealing section of the sample preparation.

A.2.3 Freezing and Degassing

Removal of dissolved gases is the main objective of this step. Styrene monomer contains relatively large amounts of air or other gases with which it has been in contact. One effective method of removal is to freeze and remelt styrene monomers several times under high vacuum. Among the dissolved gases oxygen has a drastic inhibiting effect on the rate of polymerization and on the physical properties of the resulting polymer. There is reason to believe that the so-called thermal polymerization of styrene without an addition of catalyst is chiefly caused by the presence of small amounts of peroxides which are formed by the reaction of styrene with dissolved oxygen. Also, oxygen is well known as a free radical scavenger. Numerous investigators have reported the effect of oxygen on the polymerization reaction of styrene (22, 62).

The vacuum system available for degassing permitted eight samples to be handled at the same time. The vacuum line was a standard high vacuum apparatus, with a rotary backing pump, a mercury diffusion pump, a cold trap, a McLeod gauge and eight valved standard tapered joints, size B.14. Figure A.2.3.1 shows the schematic diagram of the system.

The complete cycle of freezing, remelting and degassing procedure is as follows:

1) the styrene sample in the vial was frozen in liquid nitrogen (15 minutes),

2) the valve of the vacuum system was opened and the vials were evacuated for 15 minutes with only a rotary backing pump.

3) liquid nitrogen was removed, valve closed, and the frozen sample allowed to warm up to ambient temperature. During this time the dissolved gases appeared in bubbles and were drawn off by the vacuum pump.

4) liquid nitrogen was put back and the 3 previous steps were repeated. During the cycle of freezing and remelting no cracking of the glass vials was observed.

5) a final evacuation at 10^{-6} mm of mercury was maintained for 20 minutes on the frozen sample.

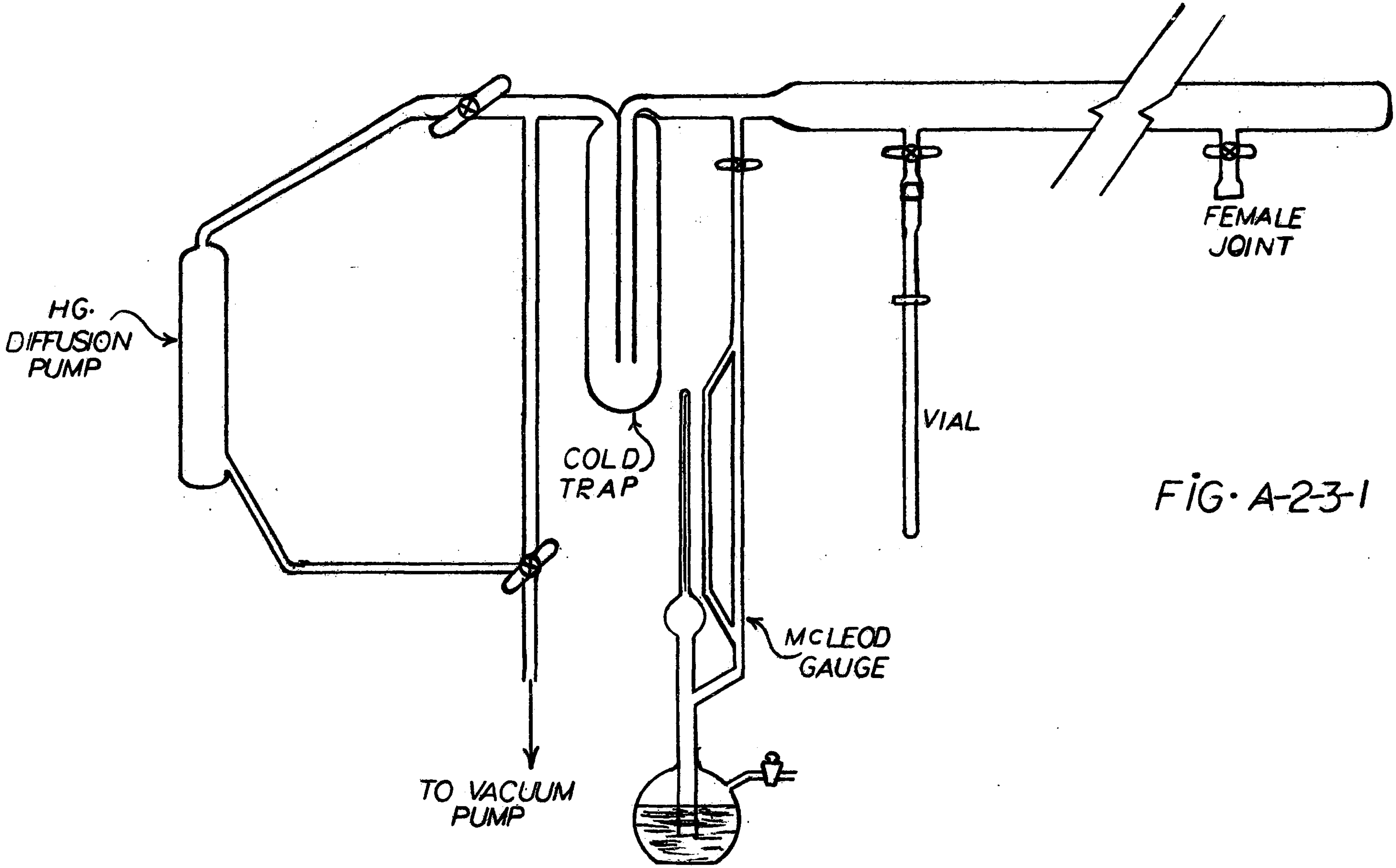


FIG. A-2-3-1

VACUUM SYSTEM FOR DEGASING

A.2.4 Sealing of the Vials

The evacuated vials were sealed by fusing the glass below the taper joint. The overall length of the vial at this stage was only 11 inches of which the sample occuppied 3 inches. After the first set of experiments, the vial geometry was altered so that the sample received a uniform dose from the source (See Figure A.2.4.1). When the vial was dropped into place in the sample holder only about 4 inches of it was immersed in the oil. The chosen temperatures were all above the boiling point of styrene monomer (145.2°C = styrene B.P.) (22). Thus distillation of styrene monomer occurred with condensation of monomer in the top part of the vial which was out of the oil bath. So, originally there was a mixture of liquid styrene monomer in the top and solid polymer in the bottom of the vial. In order to avoid this condition in subsequent experiments, the vial was sealed 4 inches from the bottom.

A.3 Sample Irradiation

Because of the high rates of polymerization which were expected at the chosen temperatures it was felt necessary to handle the samples faster and more reproducibily than the method employed by previous workers in this group.

As it is mentioned in the previous works of Dean, Elaraby and Sood (14, 15, 16) for starting the sample irradiation step they first positioned their samples in the air bath and then brought the

SEALED VIAL

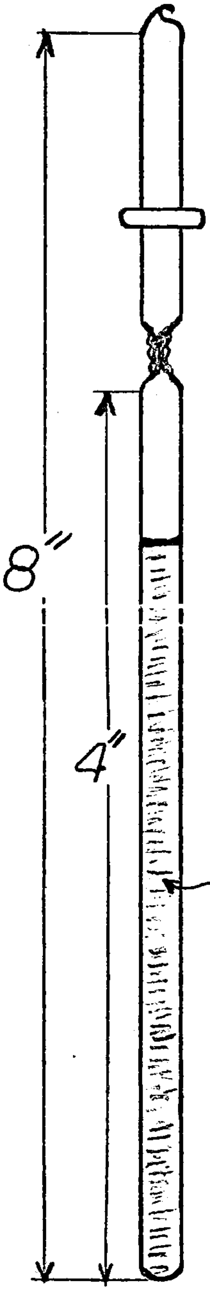


FIG A-2-4-1

Co^{60} source into position. The time between positioning of a sample in its holder and starting irradiation with the previous setting was about 12 minutes. During this time interval there was some thermal polymerization reaction in the absence of radiation which at low temperatures is negligible. As the reaction temperature increases this error becomes increasingly significant. For example, at 160°C after 12 minutes, the thermal conversion is almost 23% and at 200°C is about 68%. For kinetic study in this range of temperatures one should polyermize the samples in minutes. In order to prevent any lag of time it was decided to position the source first in its place in the oil bath and then fix the sample in its position. This could be done from outside of the hot cell and with the aid of the manipulators. A dewar flask ice bath was provided and shielded from radiation by a 4 inch lead block. Five or six samples were kept in this flask in the ice and water. With the samples in the flask and having the desired temperature in the oil bath the source was brought into position.

The marked samples were picked up by manipulators and dropped into the funnels of the sample holder. A set of three stop watches were used for recording the time. A sample vial of monomer was kept unpolymerized in the flask during each batch of irradiation for determination of the pre-irradiation polymerization in the other samples during the time which the source was up. Start and end of each reaction in every vial was recorded precisely with an accuracy of better than $\frac{1}{3}$ minutes. When the irradiation time was completed the samples were removed immediately from the reactor and dropped in the ice bath.

A.4 Determination of Conversion

A.4.1 Introduction

Several procedures have been developed for determining the amount of polymer in styrene monomer. Each method fits a specific need. For very low concentration of polymer in monomer the turbidimetry method can be used. This test is satisfactory for polymers in the range of 0.0005 to 0.25 percent by weight. The distillation gravimetric procedure is recommended where the investigator is interested in dimer, trimer and other low molecular weight materials besides polymer. The viscosity of the monomer also affords a qualitative indication of the presence of polymer. The gravimetric procedure is intended for higher concentrations of polymer and is strictly a laboratory method. These methods apply equally well to styrene derivatives, however, not all form easily filterable precipitates.

A.4.2 Gravimetric Method

This method is intended to determine appreciable quantities of polymer in styrene monomer. For most samples the vial was opened and the mixture was poured into a 150 ML pre-weighed beaker which contained small amounts of hydroquinone as an inhibitor. After adding the sample, the beaker was weighed again and the weight of polymer-monomer mixture was determined with an accuracy of better than 0.1%. Hydroquinone was added as an inhibitor because it is believed that the inhibitation of styrene polymerization by this substance is nulified in the absence of oxygen. Since benzoquinone retains its activity in the absence of oxygen, it was concluded that hydroquinone is oxidized to benzoquinone by reduction of styrene-oxygen compound which is formed in the presence of oxygen, thus preventing catalysis. The stabilization reaction then takes place between the activated styrene, if any, and the quinone (67).

1-4 dioxane was used to dissolve the sample. The quantity of dioxane used was greater for viscous samples but in most cases was less than 60 ML. The beaker was covered with aluminum foil and allowed to stand until the polymer was completely dissolved. This requires overnight for a higher molecular weight material. After the sample had dissolved it was thoroughly mixed and poured with vigorous stirring into 600-800 ML of dry methanol in a 1000 ML beaker. The small beaker was rinsed with an additional 50 ML of methanol which is added to the contents of the large beaker. The operation was properly carried out, so that there was no polymer left in the small beaker.

The mixture was left overnight until the precipitate had coagulated and settled to the bottom of the beaker. The precipitate was filtered off on 50 ML pyrex glass crucibles. A large portion of methanol was decanted and the solids were then transferred to the filter. In transferring and washing the polymer nearly 125 ML of dry methanol was used.

Although polystyrene is insoluble in methanol it is probable that the dimers, trimers and other low molecular weight polymers would be soluble (38). The precipitate was dried for at least 18 hours in a vacuum oven at 50°C.

The crucible was allowed to cool in a desiccator and was then weighed. Subsequent redrying and reweighing of the precipitate showed no significant change indicating that the drying procedure was satisfactory. Percent conversion was determined.

The accuracy of the gravimetric method is good up to nearly 95% conversion but beyond this level of conversion one should use other procedures such as ultraviolet spectrophotometry to determine residual monomer (38, 21, 18, 15). This method will be completely explained in the next section.

A.5 Spectrophotometric Analysis for Residual Monomer in Polystyrene (Determination of Conversion Beyond 95%)

A.5.1 Introduction

The pronounced effect of residual monomer on the physical properties, molding characteristics and application in food packaging of commercial polystyrene makes the determination of residual monomer in the polymer important. The determination of conversion beyond 95% by gravimetric methods is not accurate enough to distinguish the difference of conversion of about 0.5% and under. This has been reported by other workers also (15, 16, 18).

On account of the retention of styrene by polystyrene, especially by large particles, the usual determination of total volatile matter by treatment with heat and vacuum often gives low results. In a single determination, the frozen benzene technique of Lewis and Mayo (56) removed the styrene quantitatively but left in its place a few tenths of a percent of benzene.

Based on the fact that styrene has an ultraviolet radiation absorption peak at a wave length of 245 mμ, a rapid and accurate method for the determination of monomeric styrene in a polymer-monomer system was developed by several workers (57, 21).

At this wave length styrene has nearly 100 times the absorption of polystyrene. Therefore, conditions are favourable for the determination of small amounts of residual styrene in polystyrene and consequently determination of conversions beyond 95% by absorption measurements in this spectral region. It has been claimed (57) that the accuracy of this method is around ± 0.02%.

A.5.2 Principles

Spectroscopy is one of the calorimetric methods of analysis. The quantitative relationships between the composition and physical arrangement of the test solution and the fractions of incident light absorbed may be expressed mathematically by Lambert and Beer's laws. The Lambert law relates the ratio of the intensity of light transmitted by a medium to the intensity of light incident upon that medium to the thickness of that medium. There are no known exceptions to the Lambert law.

The Beer law deals with solutions of solutes which absorb light and relate the ratios of the intensity of light transmitted by a solution to the intensity of light incident upon that solution to the concentration of the solute.

The Beer law is generally applicable only to solutions of relatively low concentrations of solutes, as the activity coefficients generally decrease from unity as the concentration is increased.

The combination of these two laws serves as a basis for much of the calorimetric analysis. This law may be stated mathematically as

$$\log \frac{I_0}{I} = abc$$

a, b, c, I and I_0 are absorbancy coefficient, thickness of sample, concentration of sample solution, intensity of light transmitted through the system and the intensity of light falling upon the system respectively. The quantity ($\log_{10} I_0/I$) is often designated the absorbance and given the symbol (A). Transmittance can be defined as

$$T = I/I_0$$

$$A = \log 1/T = a.b.c.$$

The Lambert-Beer law is applicable, of course, only when its component parts are applicable. Since there are no known exceptions to the Lambert law, all apparent inapplicabilities of the combined law are due to the concentration factor. If the absorbance of a compound is directly proportional to the concentration, the compounds follow the combined law. In this case it is possible to substitute values in the equation and to determine mathematically the concentration of a compound by comparing its absorbance with the absorbance of the same compound at known concentration. If the absorbance of a compound follows the Lambert-Beer's law, a plot of the data in terms of absorbancy, A versus concentration c, yields a straight line passing through the origin. More often than not, a plot of data over a wide range of concentration of a coloured ionic solute yields a graph such as that of Figure A.5.2, signifying that the law is applicable only up to concentration c_1.

More details about the photometric error in concentration resulting from instrumental error of the absorbance measurement can be found in references (18, 58), and in most of the quantitative chemical analysis books (59).

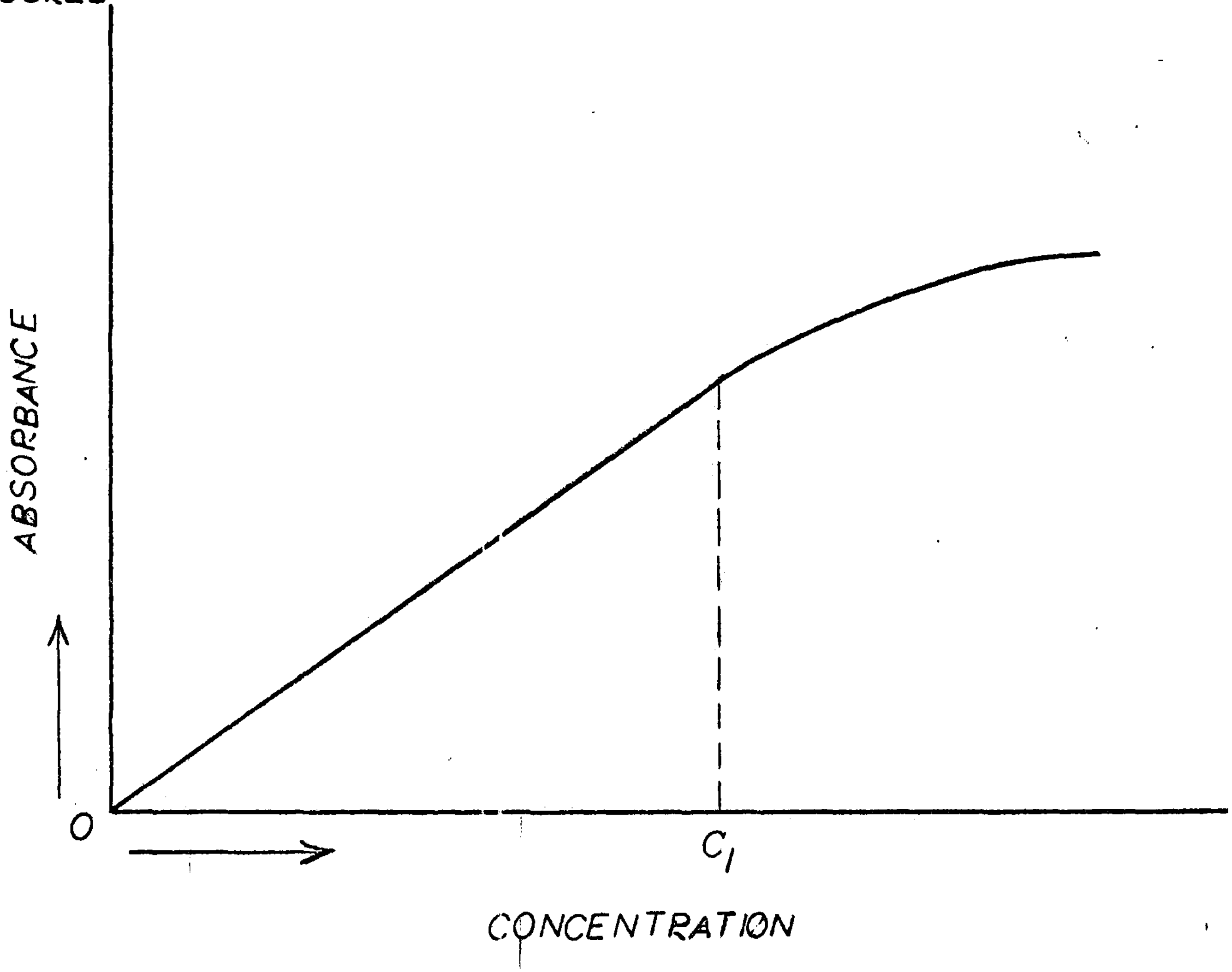
The error analysis (18) indicates that one should always adjust the concentration of the sample solution such that its transmittance falls between 0.1 to 0.7 (corresponding to absorbance values between 1 and 0.15).

A.5.3 Equipment and Method of Analysis

The apparatus was a Beckman Model DK-1A spectrophotometer. This model utilizes a single beam of energy which is chopped into alternate reference and sample beams to provide a double beam system within the sample compartment. The apparatus is able to record percent transmittance, absorbance, or energy versus wave length

TYPICA CALIBRATION
CURVE FOR A COLOURED
IONIC SOLUTE

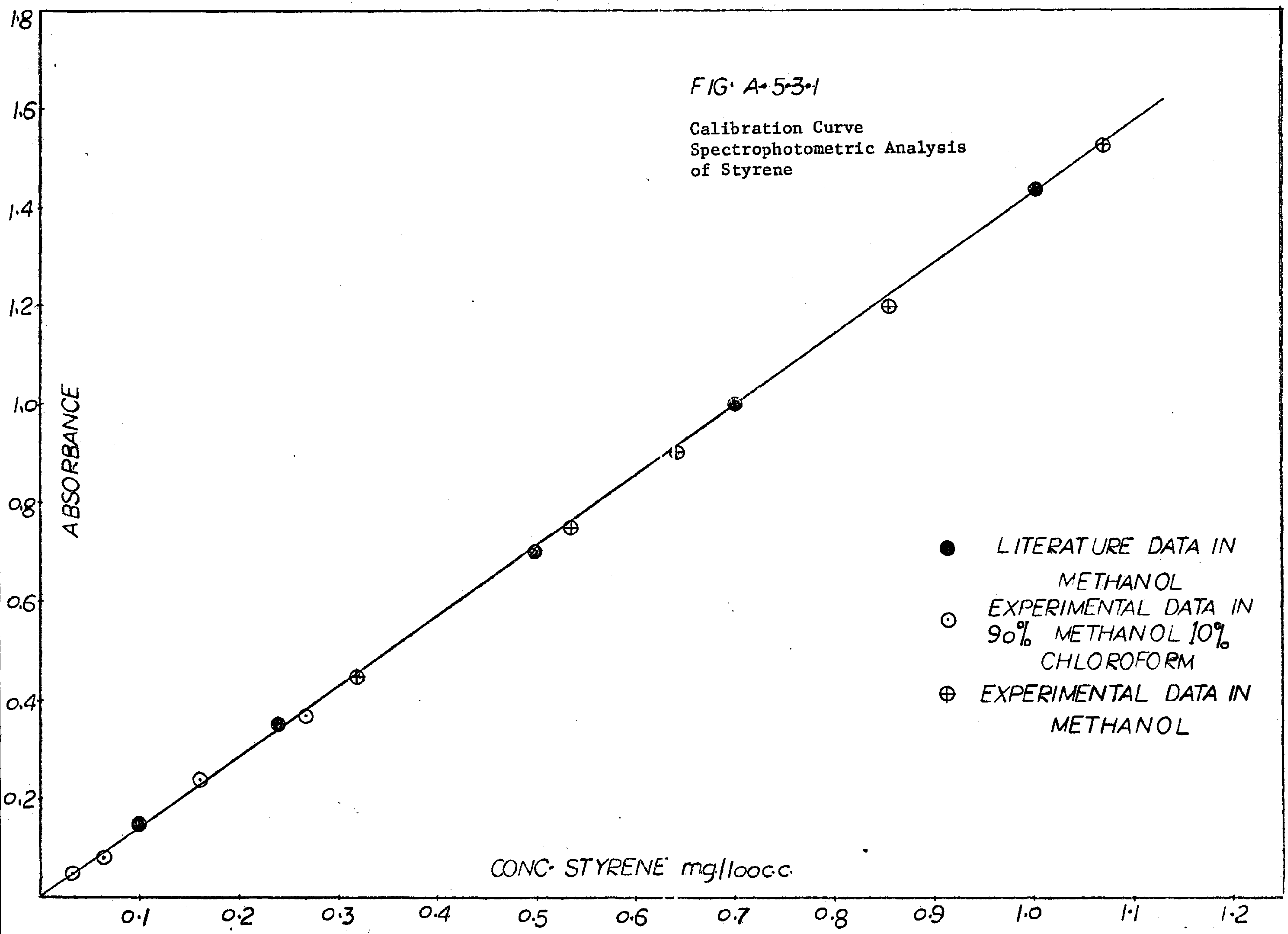
FIG· A-5-2



continuously over a wide range from below 185 mµ up to 3500 millimicrons. Radiation is provided in the wave length range below 375 mµ by a hydrogen lamp; a tungsten lamp is used in the 320-3500 millimicron wave length range. Two absorption cells of 1 cm path length rectangular with the thickness of 1 cm made from silica were used. For more specifications and operation instructions the spectrophotometer manual is recommended (58).

Eisenbrand et.al. (57) have suggested the following method for U.V. spectrophotometric analysis of residual styrene monomer. As it was mentioned before, Beer's law has some inapplicabilities due to the concentration factor and the error analysis shown (18) that one should adjust the concentration of sample in solution such that its transmittance falls between 0.1 to 0.7 corresponding to absorbance of 1 to 0.15. The minimum error for concentrations occurs at absorbance of 0.37 or transmittance of 0.43 (18). This is corresponding to a styrene concentration of 0.3 mg/100 ML (from calibration curve Figure A.5.3.1). Based on this fact the following table was prepared, which will provide the weight of polymer samples at various conversions corresponding to the desired range of absorbance or transmittance.

In order to have a suitable solution sample one has to know the conversion of the sample fairly accurately. With the consideration of gravimetric results this condition can be achieved easily. The detailed procedure of sample preparation and analysis was done as follows:



FIG· A·5·3·1

Calibration Curve
Spectrophotometric Analysis
of Styrene

TABLE A.5.3.1

% Conversion	% Styrene	Recommended wt. of sample
10	90	1.67 mg
20	80	1.88
50	50	3.0
70	30	5.0
90	10	15.0
95	5	30.0
98	2	75.0
99	1	150.0
99.5	0.5	300.0
99.9	0.1	1500.0

1) the required weight of the samples were measured accurately and transferred into a 50 ML volumetric flask containing 30 ML analytical grade chloroform. The solution was allowed to sit overnight to ensure the dissolution of the polymer present. It was then made up to volume with the addition of chloroform.

2) 10 ML of the above solution was added slowly into 90 ML of analytical grade methanol (delivered accurately by a burette) into a 150 ML beaker to allow the precipitation of polymer.

3) the resulting mixture was then filtered through a 50 ML coarse sintered glass crucible, and the filtrate was the sample solution for absorption measurement.

4) reference solution was a 10% chloroform in methanol (both reagent grade) which was prepared similarly to the sample solution preparation.

5) the absorbance and transmittance of the sample were both measured at 245 mμ. The concentration of styrene (C mg/100 ML) in the sample was determined from the standard calibration curve (prepared by Eisenbrand et.al (57).

6) Mg of styrene in sample = 5 C (5 is the dilution factor $\frac{50}{10} = 5$.

Percent of styrene in sample = $\frac{5\ \text{C (mg)}}{\text{wt. of sample (mg)}} \times 100$

Therefore, percent conversion = 100 - percent of styrene in the sample

A.5.4 Results and Discussion

By the above method styrene monomers were detected in different samples which have conversion beyond 90%. The results of polymer samples are given in Table A.5.4.1. It has been tried to have absorbance-transmittance values in the desired range.

All absorbance and transmittance were read at 245 mμ. At this wave length the presence of impurities such as benzene, toluene, ethylbenzene, diethylbenzene and so forth, seems not to interfere greatly unless they occur in quantitites greater than that of the styrene present. The above substances have roughly 10% of the absorption of styrene at 245 mμ. If the impurities are ethylvinylbenzene or divinylbenzene, then ultraviolet absorption is not satisfactory because while the absorption of the former is about the same as that of styrene, that of divinylbenzene is about ten times as much at about the same wave lengths. The 245 mμ was chosen because it was assumed that there were no such impurities. Another objection to this method can be related to incapability of the technique in the case of unknown converted samples which would require trial and error to obtain an acceptable concentration.

Also, the method is not sensitive enough for low conversion samples as it requires too small amounts of sample. As is clear from Table A.5.3.1, conversions beyond 99.9% are difficult to measure because of high polymer concentrations.

In summary, the spectophotometric method of analysis of polystyrene for residual monomer has several advantages and some limitations. No treatment of sample other than solution is required. The method is rapid, and has precision and accuracy suitable for measurements at high conversion if the conversion of sample isknown to lie ± 0.1%. This method is applicable also for quality control.

TABLE A.5.4.1

Results of U.V. Spectrophotometric Measurements

Sample No.	Sample wt. (mg)	A Absorbance	T Transmittance	% CONVERSION		
				From A	From T	Average
A1R18	14.6	0.53	0.295	87.40	87.41	87.4
A1R19	28.44	0.545	0.285	93.25	93.15	93.2
A1R20	40.0	0.37	0.418	96.78	96.82	96.8
A1R21	152.12	0.30	0.501	99.30	99.34	99.3
A1R22	148.8	0.26	0.549	99.39	99.42	99.4
A1R23	152.15	0.20	0.631	99.53	99.48	99.5
A1R24	307.16	0.28	0.531	99.69	99.70	99.7
A1R25	310.29	0.20	0.631	99.78	99.81	99.8
A2R8	17.6	0.69	0.204	86.24	86.4	86.3
A2R9	26.8	0.45	0.355	94.12	94.1	94.1
A2R10	31.4	0.29	0.513	96.82	96.80	96.8
A2R11	101.5	0.24	0.575	99.16	99.48	99.3
A2R12	109.0	0.21	0.616	99.28	99.53	99.4
A2R13	107.3	0.18	0.661	99.42	99.63	99.5
A2R14	105.0	0.13	0.741	99.59	99.74	99.6
A2R15	113.0	0.09	0.812	99.71	99.82	99.8
AT21	22.43	0.415	0.384	93.57	93.62	93.6
AT22	62.71	0.53	0.295	97.05	97.1	97.0
AT23	76.92	0.45	0.355	97.91	98.1	98.0
AT24	145.13	0.42	0.380	99.0	99.1	99.0
AT25	148.3	0.345	0.452	99.2	99.21	99.2
B1R9	18.26	0.445	0.359	91.40	91.82	91.6
B1R10	45.4	0.475	0.335	96.32	96.10	96.2
B1R11	93.2	0.45	0.355	98.30	98.28	98.3
B1R12	234.13	0.43	0.371	99.36	99.43	99.4
B1R13	300.22	0.74	0.182	99.14	99.89	99.5
B1R14	301.43	0.32	0.478	99.64	99.76	99.7
B1R15	302.14	0.26	0.549	99.70	99.91	99.8
B2R9	17.25	0.475	0.335	90.41	91.60	91.5
B2R10	43.14	0.6	0.251	95.11	95.8	95.48
B2R11	100.13	0.575	0.266	98.0	98.28	98.14
B2R12	295.43	0.52	0.302	99.39	99.40	99.4
B2R13	298.14	0.33	0.468	99.61	99.47	99.54
B2R14	300.24	0.235	0.582	99.73	99.76	99.75
B2R15	304.13	0.09	0.812	99.90	99.91	99.9

Continued....

TABLE A.5.4.1

(Continued)

Sample No.	Sample wt. (mg)	A Absorbance	T Transmittance	% CONVERSION		
				From A	From T	Average
BT11	19.8	0.32	0.478	94.5	93.80	94.1
BT12	20.2	0.29	0.513	95.1	96.0	95.5
BT13	26.8	0.26	0.549	96.6	95.91	96.2
BT14	65.2	0.53	0.295	97.15	97.1	97.1
BT15	100.4	0.52	0.302	98.21	97.91	98.05
BT16	102.1	0.45	0.355	98.41	98.59	98.5
C1R11	24.1	0.48	0.468	93.21	93.60	93.4
C1R12	85.4	0.31	0.488	98.74	98.94	98.8
C1R13	59.1	0.238	0.579	98.61	98.87	98.8
C1R14	80.0	0.108	0.778	99.53	99.56	99.6
C1R15	157.0	0.108	0.778	99.76	99.77	99.8
C1R16	172.6	0.09	0.812	99.92	99.83	99.9
C1R17	310.0	0.088	0.816	99.91	99.91	99.91
CT12	25.5	0.56	0.275	93.32	92.1	92.2
CT13	34.9	0.36	0.436	94.31	94.35	94.3
CT14	30.7	0.33	0.468	96.73	96.68	96.7
CT15	70.8	0.28	0.531	97.90	97.91	97.9
CT16	75.0	0.33	0.468	98.48	98.42	98.4
D1R10	18.22	0.52	0.302	90.19	90.21	90.2
D1R11	52.28	0.545	0.285	96.40	96.52	96.4
D1R12	181.0	0.415	0.383	99.20	99.21	99.2
D1R13	300.17	0.13	0.741	99.85	99.90	99.9
D1R14	301.23	0.07	0.852	99.92	99.94	99.93
D1R15	324.5	0.00	1.00	100.0	100.0	100.0
D1R16	320.5	0.00	1.00	100.0	100.0	100.0
D2R9	16.7	0.445	0.359	90.72	90.9	90.8
D2R10	50.21	0.53	0.295	96.31	96.34	96.3
D2R11	164.0	0.39	0.407	99.18	99.21	99.2
D2R12	300.42	0.08	0.832	99.91	99.90	99.91
D2R13	304.23	0.062	0.867	99.93	99.91	99.92
D2R14	322.15	0.048	0.895	99.95	99.96	99.95
D2R15	323.1	0.00	1.00	100.0	100.0	100.0
DT12	15.21	0.275	0.531	93.82	93.79	93.8
DT13	42.15	0.575	0.266	95.23	95.4	95.3
DT14	42.0	0.45	0.355	96.23	96.18	96.2
DT15	42.4	0.43	0.371	96.40	96.41	96.4
DT16	70.3	0.545	0.285	97.32	97.31	97.3

APPENDIX B

Dosimetry

B.1 Introduction

When high energy radiation is used to produce a change in matter whether a physical change, as in the testing of materials for use in reactors, or a chemical change, as in the polymerization of plastics, the radiation must be measured and controlled. The measurement of radiation in situations such as these constitutes the subject of radiation dosimetry.

When a beam of radiation traverses matter three types of physical information may be of interest.

1) The spectral distribution of the radiation,
2) the intensity of radiation at some point,
3) the amount of energy absorbed per unit mass at a point in the irradiated material. In most applications however, what is of primary significance is not the energy in the beam but the energy absorbed per unit mass of irradiated material. A biological effect, for example, must depend on the amount of energy locally absorbed at the point in question, rather than on the amount of energy passing through this point. The radiation chemist requires to know the energy in e.V. absorbed by his system. This is a matter for radiation dosimetry.

Radiation dosimetry can be accomplished either by absolute methods or relative methods. In absolute dosimetry the absorbed dose will be measured directly. Several different methods have been used for this purpose. Calorimetry is one of the most direct methods, since it provides a direct measure of the temperature rise of a system. This cannot be done where a chemical change is induced unless the heat of reaction can be calculated. Ionization methods have been used widely in radiotherapy. In this method with an ionization chamber it is possible to measure the total number of ions produced by the source in air in a given time. There are some principal difficulties in using ionization chambers for the dosimetry of chemical systems (34).

For relative dosimetry, once a radiation field has been explored by an absolute method of dosimetry, it is possible to calibrate other radiation indicators in this field by exposing them to a well-defined radiation dose and thereafter using the same indicator for further dose determinations. A large number of indicators have already been proposed for radiation dosimetry, based both on physical and on chemical methods. A brief description is given of some of the most important physical and chemical methods which are suitable for use in radiation chemistry.

B.1.1 Calorimetric and Photographic Methods

In calorimetric and photographic methods, a large number of solid substances such as glasses, crystals, plastics, etc. become discoloured or change colour when exposed to ionizing radiations. In principle, all these colour changes, when measured quantitatively, can be used for dosimetry. However, in order to provide a suitable dosimeter several requirements must be fulfilled:

1) the relationship between dose and optical density change should be linear and independent of dose rate.
2) the final optical density should be reproducible and stable in time after irradiation.
3) the measured change should be insensitive to external factors such as temperature and light.
4) the response should be independent of radiation quality over a wide range of energies.

A number of systematic studies have been carried out with glasses of various compositions. The stability of the discolouration after irradiation was found to improve when the glass was submitted to a standard heat treatment (66, 14).

Chemical methods are the most convenient techniques of dosimetry. This method has been considered in the present work and will be discussed in more detail in the following section. Other methods such as the calculation from source strength technique, charge collection methods and cobalt glass dosimetry can be found in detail in references (34, 14, 66), respectively.

B.2 Principles

The chemical dosimetry method is to irradiate in the place of the system of interest a system with a known yield. From measurement of the amount of chemical change in this system it is then possible to calculate the absorbed dose, and hence the dose received by the system of interest.

One of the most significant features of chemical methods is the fact that while with ionization or calorimetric methods one is bound to introduce into the radiation field some additional absorbing substances which may actually change the irradiation geometry, a carefully chosen chemical dosimeter can often be irradiated under conditions identical to those of the system under investigation.

It should be noted that using a chemical dosimeter for determining the radiation chemical yield of another radiation chemical reaction is in fact equivalent to expressing the yield of the chemical system under investigation with reference to the yield of a well-known standard reaction which has been thoroughly investigated. It is desirable that a system to be used for dosimetry should satisfy the following criteria.

1) the chemical change brought about by the absorption of a given radiation dose should be independent of
    i) the concentration of the active substance and of the final product throughout a broad range
    ii) radiation dose-rate
    iii) radiation quality

   iv) any further changes which may occur during the reaction such as pH changes, concentration changes, the formation of gases, etc.

2) The chemical requirements are:

   i) easy analytical determination of chemical change
   ii) the possibility of using ordinary 'ANALAR' reagents, without further purification.
   iii) adequate stability of the solutions under ordinary storage conditions at room temperature and in the presence of air and light.
   iv) the mean atomic number should be close to that of the system of interest.

So far, no system has been found which meets all these requirements. Several systems are, however, close enough to the ideal dosimeter to lead to important practical applications.

The chemical reaction which has been studied most extensively for dosimetry purposes is the radiation-induced oxidation of aerated solutions of ferrous ammonium sulphate in nearly 0.1 N sulphuric acid. Some workers used 0.8 N sulphuric acid, but 0.1 N is closer to water in mean atomic number. The ferric yields in the two systems are the same to within 3%.

Chapiro has suggested the oxidation yield of 15.6 ± 0.5 for gamma rays of quantum energies above 100 K.e.V. The yields are expressed in terms of $G(Fe^{3+})$ values. The definition of "G Value" has been given in the previous sections.

In order to obtain satisfactory results with the ferrous-ferric ion dosimeter it is important to satisfy a number of experimental requirements. The most important precautions to be observed are:

1) use of highly cleaned irradiation cells and dishes for handling the dosimetric solution,
2) avoiding contamination by traces of organic substances,
3) preventing oxygen depletion in the solution during irradiation, or in other words, care must be taken that oxygen is not exhausted locally in the solution,
4) water should be distilled from alkaline permanganate because the most troublesome impurities in the water are organic and these cannot be removed by distillation or passage through ion-exchange resins.

Spectrophotometric analysis could be used as an accurate method of determination of the ferric ions formed. The usual wave length used is 304 mμ, the maximum in the optical absorption curve. The absorbed dose rate received by a ferrous sulphate solutions may be calculated from the formula

$$\text{Absorbed dose (rad)} = 2.94 \times 10^{4}(1-0.007\ t)\ \text{O.D.} \qquad \text{B.2.1}$$

or

$$\text{Absorbed dose(eV/g)} = 1.84 \times 10^{18}(1-0.007\ t)\ \text{O.D.} \qquad \text{B.2.2}$$

where O.D. is equal to optical density of irradiated solution at 304 mμ measured in 1 cm cells with unirradiated solution as blank and t = temperature in °C at which O.D. was measured minus 20°C.

To calculate the absorbed dose one should consider that energy absorption in one system can be related to energy absorption in another system by comparing the "stopping power" or energy absorption coefficients of the two systems. If the dose rate D_A for system A is required and the dose rate D_B for system B is known, then

$$D_A = D_B(\frac{\mu}{\rho})_A \quad (\frac{\mu}{\rho})_B \qquad \text{B.2.3}$$

will relate the two dose rates, where $(\frac{\mu}{\rho})$ is the mass energy absorption coefficient of each system. Mass energy absorption coefficients for any material are a function of the photon energy of the radiation.

For a given photon energy, the mass energy absorption coefficient for any compound X_mY_n is given by

$$(\frac{\mu}{\rho})X_mY_n = m\,W_X(\frac{\mu}{\rho})_X + n\,W_Y(\frac{\mu}{\rho})_Y \qquad \text{B.2.4}$$

where $(\frac{\mu}{\rho})_X$ and $(\frac{\mu}{\rho})_Y$ are the mass energy coefficients of elements X and Y, W_X and W_Y are the weights of element X and Y divided by the total molecular weight of the compound, and m and n represent the number of times each element occurs in the compound. The value of $(\frac{\mu}{\rho})$ for some elements and compounds are given by (60).

After all, this chemical dosimetry method is more accurate in the range of total dose of 1×10^{18} eV/g to 2.4×10^{18} eV/g.

B.3 Equipment and Method of Analysis

B.3.1 Equipment

A U.V. spectrophotometer model DK-1A was used for analysis of the samples. This model utilizes a single beam of energy which is chopped into alternate reference and sample beams to provide a double beam system within the sample compartment. For more information about the specifications and methods of operation the reader is referred to (58, 59).

B.3.2 Sample Preparation

A dosimetric solution consisting of 0.001 M ferrous ammonium sulphate, 0.001 M sodium chloride and 0.4 M sulfuric acid was prepared using distilled water obtained by double distillation from an alkaline permanganate solution which was prepared by adding a few pellets of NaoH to a liter of 0.1 N KMno4. For convenience a stock solution of 0.5 M in Fe^{++} (ferrous ammonium sulphate) and 0.5 M in sodium chloride was prepared first because this solution can be stored for up to 3 months (30).

When the test was to be run, 2 ML of the above stock solution was added to 1 liter of a solution of 0.4 M sulfuric acid that had been saturated with oxygen during the same day. For introducing the oxygen a clean dust free glass tubing with a special porcelain bubbler attached was used. The saturation of the solution with oxygen was conducted for several hours before filling the same experimental vials (reaction vials, section A.1.2) with this solution. Several vials were filled with the solution and used for irradiation.

All containers in this experiment were cleaned with chromic-sulfuric acid cleaning solution and rinsed thoroughly three times with distilled water. Extreme precautions were taken in order to prevent any contamination of the glassware with organic substances, dust and copper materials. It should be mentioned here that all reagents were analytical grade.

B.3.3 Sample Irradiation

Several vials identical to those used for the polymerization reaction were cleaned carefully and filled with approximately 1.5 cc of dosimetric solution (Fricke solution). From previous data prepared by Elaraby (15) the source strength was known to be approximately 50 rad/sec at a 4 inch distance and 20 rad/sec at a 6 inch distance, which require that the Fricke solution be exposed for a maximum of 270 seconds in $3\frac{3}{8}$ inches distance (1st slot in sample holder) and 330 seconds in a 6 inch distance, so it would not receive more than the allowable maximum dose. In estimation of the above required times the 'make ready' time for moving the samples in and out of the radiation field have been considered.

The same procedure as in sample irradiation step A.3 were used here for positioning and irradiating of Fricke solution, except that this experiment was conducted at ambient temperature.

B.3.4 Analysis

After the irradiation time was completed the samples were removed from the radiation field and the contents of the vials were poured into the 1 cm matched quartz cell of the U.V. spectrophotometer by the use of a thoroughly cleaned long needled hypodermic 10 cc syringe. The optical density of the specimen was determined by scanning the sample from 310 mμ to 300 mμ and using the reading at 304 mμ. A portion of unirradiated ferrous solution was used as a blank in the spectrophotometer. Also, unirradiated Fricke solution was run between each irradiated sample to reset the base line. All of these measurements were made in the same day.

B.4 Results and Discussion

The measured optical density of the irradiated sample which is actually the ferric ion concentration can be converted to absorbed dose using the formula in B.2.1. The results are given in Table B.4.1.

These experimentally determined dose rates are the absorbed dose in water. For calculation of the absorbed dose in styrene, equation B.2.4 was used. The value of mass-energy absorption coefficient $(\frac{\mu}{\rho})$ for styrene and water were obtained from (60).

For styrene (C_8H_8) $\frac{\mu}{\rho} = 0.02876$

For water (H_2O) $\frac{\mu}{\rho} = 0.02970$

Then the absorbed dose in styrene is given by

TABLE B.4.1

Dose Rate from Fricke Dosimetry

Sample No.	Distance inches	Total Irradiation Time (sec.)	O.D. (Absorbance)	Total Absorption Dose Rad	Dose Rate Rad/sec.	Ave. Rad/sec.
1	$3\frac{3}{8}$	270	0.498	1.4129×10^4	52.33	51.91
2	$3\frac{3}{8}$	270	0.490	1.3902×10^4	51.49	
3	6	330	0.235	0.6667×10^4	20.63	20.42
4	6	330	0.24	0.6809×10^4	20.20	

At $3\frac{3}{8}$ inches distance:

$$\text{Dose rate/styrene} = 51.91 \times \frac{0.02876}{0.02970} = 50.27 \text{ Rads/sec}$$

At 6 inches distance:

$$\text{Dose rate/styrene} = 20.42 \times \frac{0.02876}{0.02970} = 19.77 \text{ Rads/sec}$$

The results of Fricke dosimetry method can have an estimated probable error up to 5%. This error can be caused by short time of irradiation and especially the presence of impurities.

Small quantities of impurities can exert a powerful influence on radiation induced reactions. A 10^{-3} M aqueous solution might, if care were not taken, contain more impurity than solute, leading to spurious results. But, if the necessary precautions were taken into account in preparation of the sample solutions and analysis, this method can be applied to any radiation geometry and to any type of radiation cell. Moreover, no effect on accuracy of the measurement of radiation dose is observed up to rates of 10^7 rads/hr.

The accuracy of this method is not significantly changed by varying temperature of the system between 0 to 50°C during irradiation. Also, this method has been shown to be independent of energy in the range of 0.1 to 2 MeV. It thus appears that chemical methods of dosimetry provide unique features of great importance to the chemist and this accounts for their increasing popularity in most radiation chemical studies.

APPENDIX C

Gel Permeation Chromatography (G.P.C.)

C.1 Introduction

Synthetic high polymers are a mixture of compounds prepared from the same monomer or monomers but of a range of molecular weight. Although the chemical structure of the repeating units is of first importance in governing the properties of a polymer, the flow of the polymer is influenced strongly by its average molecular weight. In practice, a knowledge of the average molecular weight is needed to understand the behaviour of the polymer in extrusion, in film forming, and in many other methods of fabrication. In research these characteristics are needed to define samples for precise physical and mechanical measurements and to define products in polymerization kinetics studies. In order to establish such an experimental regime, it is necessary to perform hundreds of analyses of molecular weight distribution. There are several useful methods for the determination of average molecular weights, but until the recent development of Gel Permeation Chromatography (G.P.C.) there were hardly any practical methods for the determination of the distribution of molecular weights.

One of the most successful methods in the determination of M.W.D. is Gel Permeation Chromatography (G.P.C.). Because of its ease of operation and success in a large range of molecular separations, G.P.C. has gained quick and wide acceptance by polymer chemists in many fields.

The commercial G.P.C. was first introduced by Waters Associates Inc. in 1963.

Since the first paper published by Moore (53) in 1964 on the G.P.C. there have appeared already, a large number of articles dealing with the mechanism of G.P.C. separation, interpretation of the G.P.C. chromatogram, and examples of its application. Most of this information can be found in (14, 18, 52, 54).

This technique is discussed here because it was decided that molecular weight distribution might have an important bearing on the elucidations of high temperature polymerization.

This investigation was aimed at finding out the differences, if any, between the average molecular weights of the produced polymers. Twenty-eight samples were studied of which 18 were analyzed by the Polymer Corporation Laboratories, Sarnia, Ontario and the rest in our laboratories.

C.2 Principles

Gel Permeation Chromatography is a term which was introduced in 1964 by J. Moore of the Dow Chemical Company to describe the technique of molecular size separation accomplished on a gel column using liquid chromatography apparatus. The term gel permeation is derived from the method of separation on a column consisting of highly cross-linked polystyrene gel with a liquid structure. Separation then occurs on the basis of the permeability of the gel. Molecules smaller than the maximum pore size enter the gel and molecules larger than the maximum pore size pass through the column in the interstitial volume. So, separation is according to their size. The smaller molecules require more solvent to elute them through the column. Also, separation takes place in a limited volume of column packing and depends largely on the size and availability of the pores of the packing material. To obtain an M.W.D. usually expressed as the weight fraction of each molecular species versus chain length or molecular weight, a separation of species must be obtained on the basis of a property that is a function of M.W. or chain length. Fractionation makes use of the solubility variation with molecular weight. Ultra-centrifugation makes use of the weight variation with M.W. Gel Permeation Chromatography makes use of the molecular size variation with molecular weight.

A dilute solution of the polymer in the tetrahydrofuran carrier solvent is injected as a pulse at the inlet of the column into the continuous carrier solvent stream. As the polymer molecules flow through the column they diffuse into the gel pores, permeating the gel to varying degrees depending on their molecular size in the solution. Since the larger molecules can enter fewer pores and cannot penetrate as far as the smaller molecules, they move more rapidly through the columns. Thus the largest molecules are eluted first, followed by successively smaller molecules.

The concentration of the eluting species can be monitored with a suitable detector. By knowing the relatioship between elution volume and M.W. the resulting chromatogram of concentration versus elution volume can be converted to an absolute M.W.D. if the resolution is perfect. A detailed discussion of the operation of the G.P.C. and interpretation of the data can be found in references (18, 52).

C.3 Description of the Apparatus

The G.P.C. which was used in this investigation was a standard Waters Units Model 100. This unit consists of the following sections:

Solvent system,
Sample Injection system,
Column system,
Detector,
Recorder, and
Digital translator.

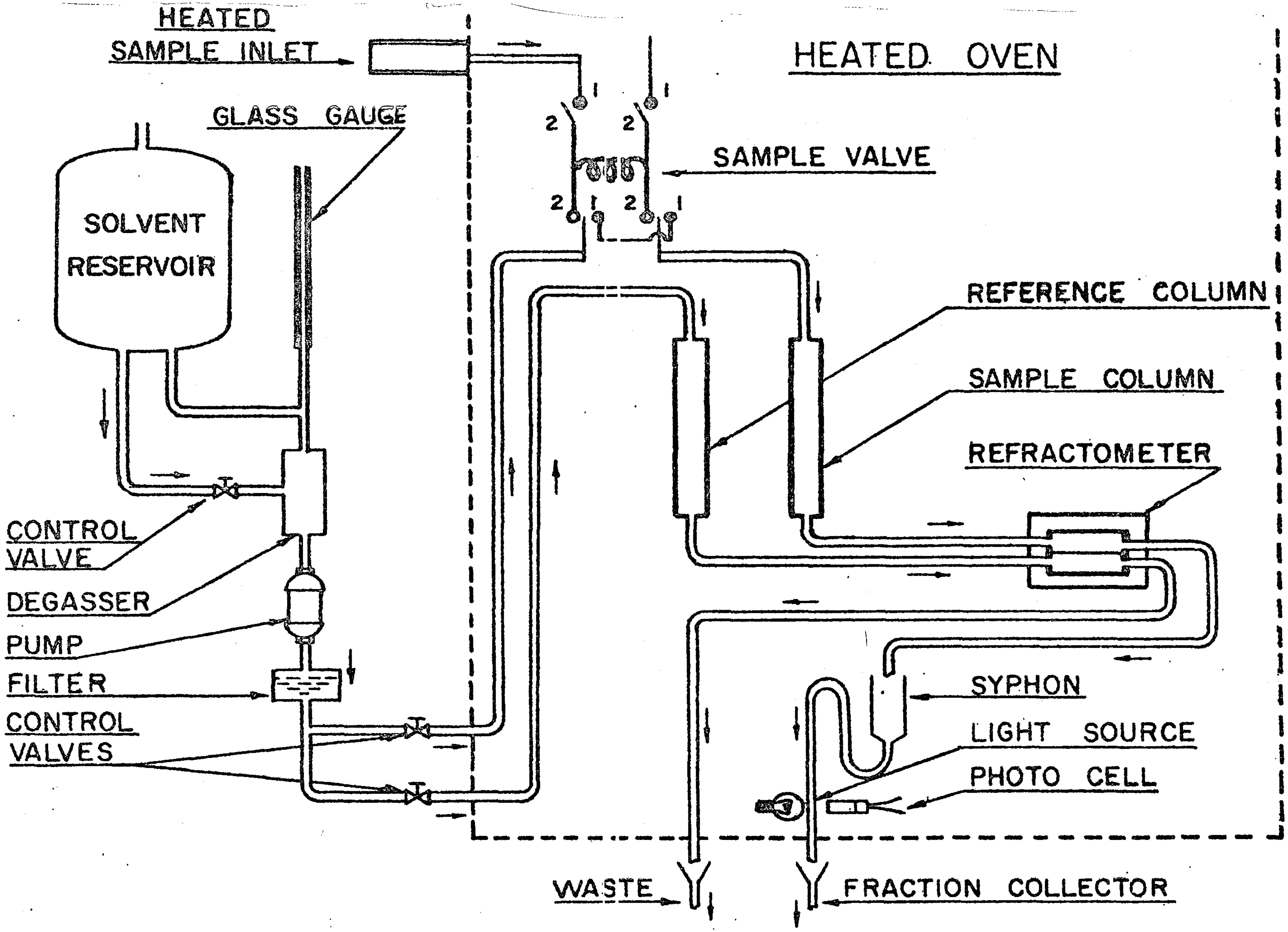
The solvent system consists of a solvent reservoir, a solvent degasser, a variable stroke positive displacement pump which pulses to provide a constant and controlled solvent flow rate. The sample injection system consists of a four-port valve. The column system consists of one to five columns in series. Each column is made of 4 feet lengths of $\frac{3}{8}$ inch stainless steel tubing packed with a cross-linked polystyrene gel and capped at each end. The concentration of polymer in the column was detected by a Water's differential refractometer, which measures the difference in refractive index between the pure solvent and the polymer solution and as a result a direct measure of polymer concentration. A digital translator converts the analog signal from the refractometer into digital form, punches a paper tape and provides a strip chart record.

Solvent was eluted at a constant rate so that retention times of samples were directly related to the amount of solvent eluted. The eluted solvent flowed continuously into the syphon. The discharge of the syphon triggers an electric signal causing an elution mark on the chart. Each elution mark or count indicates a volume of 5 ML solvent eluted. The digital translator provides an option of read-out interval of 20-240 seconds and three different output formats for heights of G.P.C. trace, injection of sample and elution marks or counts.

The punched tape output was first converted to binary cards via the IBM tape to card punch Model-46. The binary cards were converted to digital cards via the use of a Macro-Assembly-Program (MAP) for the CDC-6400 computer. The digital cards were then used as input data for decoding and calculation of average molecular weights and MWD. Figures C.3.1, 2, 3 shows the G.P.C. flow diagram, column cross section, and a typical G.P.C. chromatogram, respectively.

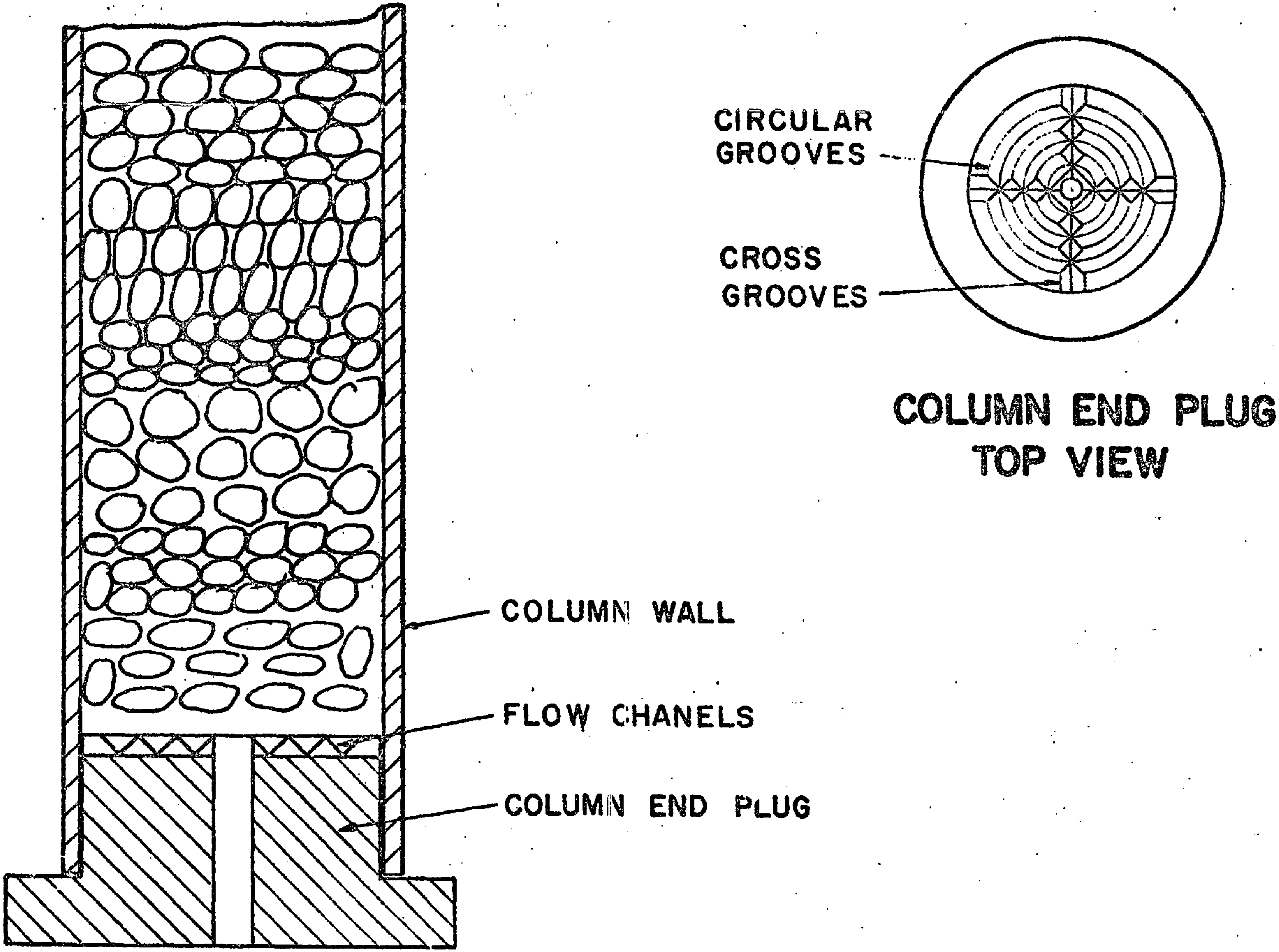
C.4 Sample Preparation

The samples for the G.P.C. were prepared by weighing 0.0222 grams of vacuum dried polystyrene into a preweighed sample bottle. These bottles were extremely clean and kept out of dust and other impurities very carefully. Nearly 12 hours before the injection, each sample was dissolved in 25 ML tetrahydrofuran (THF) which was obtained directly from the G.P.C. solvent reservoir. The solution was left in the G.P.C. room in order to reach the equilibrium temperature with the carrier solvent in the G.P.C. column. These precautions were necessary in order to reduce the errors involved in sample preparation



WATERS LIQUID CHROMATOGRAPHY ASSEMBLY.

FIG. C-3-1



COLUMN END PLUG
TOP VIEW

FIG. C-3-2

COLUMN CROSS SECTION &
END PLUG DETAIL

TYPICAL G.P.C. CHROMATOGRAM

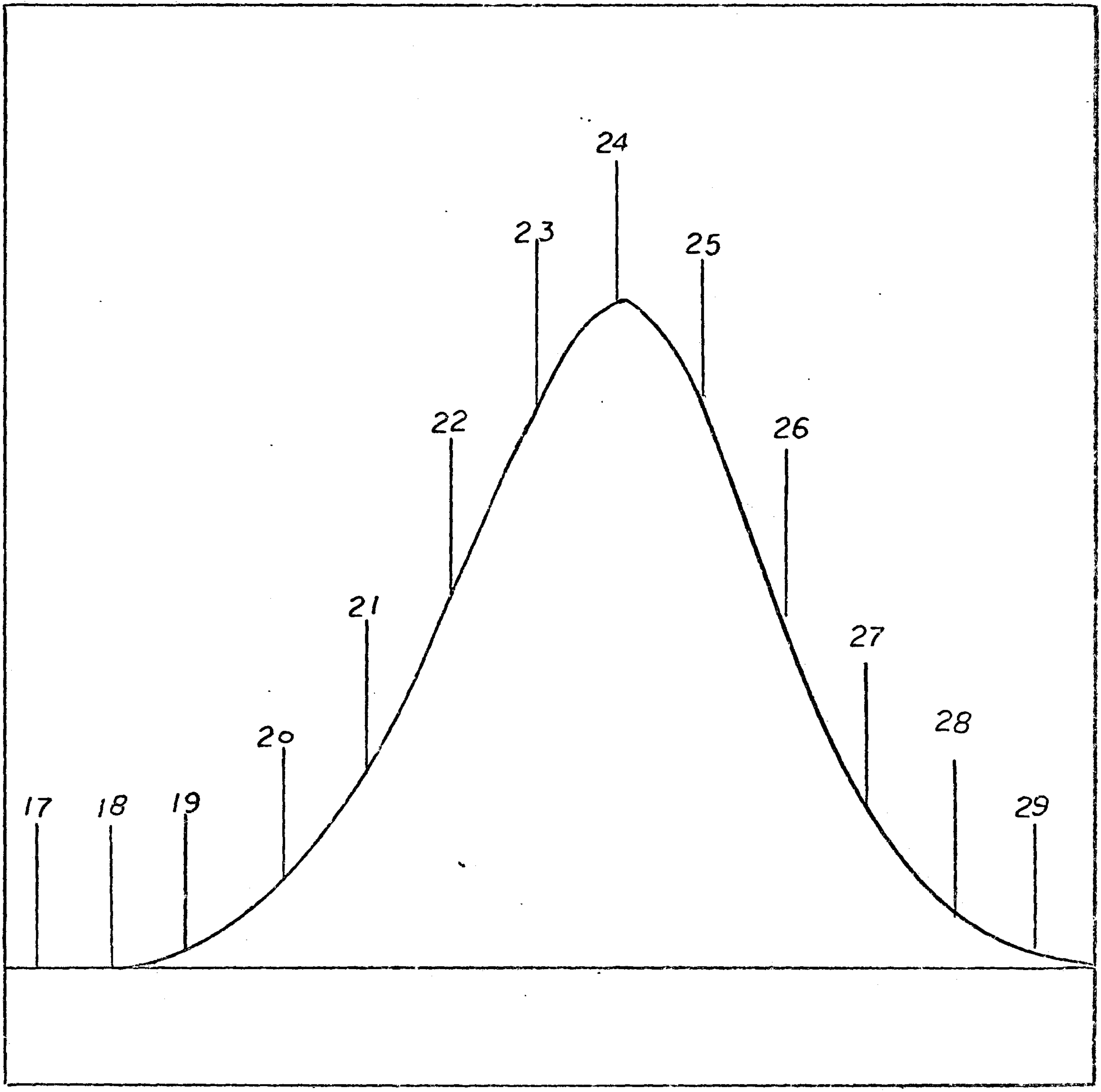


FIG. C-3-3

due to the presence of dust, condensation of water in air and other impurities.

C.5 Analysis

Because an extensive analysis of the G.P.C. data would be well beyond the scope of this chapter it was decided to consider the recommended operating conditions (52) for the rapid analysis of 10 samples with the G.P.C.. A detailed discussion of the following conditions of G.P.C. operation is given in (52, 54).

All samples were analyzed with a set of 5 columns in series. Two different column packings were used, Bioglass and Styragel. The details of column combinations are given in Table C.5.1.

Tetrahydrofuran was used as carrier solvent with flow rates of 2 ML/min. in bioglass packing and 2.5 ML/min. in styragel column.

The volume of solvent discharged through the syphon in each count was 4.47 ML. Operating temperature was 30°C ± 1°C. 2 ML of each sample was injected into the G.P.C. The injection should be done after the discharge of the syphon which the teletype will print a 4 digit number started with 7. As soon as the valve has been set at the injection position the teletype will print a four digit number starting with 4. Closing the sample loop valve is done by putting it in the closed position again after the second discharge of the syphon. In other words, the injection of the sample should be done inbetween two successive counts.

TABLE C.5.1

Description of Column Combinations and Conditions

wt.% Sample Conc.	Amount Injected	Column Combination Porosities in Angstroms	T.H.F. Flow Rate	Temp. °C
0.25%	2 ML	1x2500, 2x500, 1x1000 1x500, 2x200	2 ML/min.	34°C
0.1%	2 ML	$5x10^6$, $5x10^6$ ($7x10^5$, $5x10^6$), 10^4, 800	2.5 ML/min.	30°C±1°C

The figures for the second column is the chain length of the styragel.

C.6 Results and Discussion

This analysis was a very brief study of the number average and weight average molecular weight of 28 polymer samples produced by two different methods of polymerization, i.e., thermal polymerized and (thermal + radiation) polymerized polystyrene.

Due to the difficulties which arose from the plugging of the G.P.C. column 18 samples were analyzed by a different G.P.C. arrangement. As expected, the results of those analysis are somewhat higher than those which were analyzed here.

Regardless of the different conditions of analysis the consistency of the results are quite remarkable. The molecular weights of the samples ranged from 96,000- 320,000 for MW and 52,000 - 124,000 for M_n.

The results of molecular weight averages of all the polymer samples are given in Table C.6.1.

TABLE C.6.1

Molecular Weight Averages

Sample No.	Column Code	Uncorrected Results		
		$M_W \times 10^{-5}$	$M_N \times 10^{-5}$	M_W/M_N
D2R4 26	1	1.79	0.75	2.39
D2R8 27	1	3.20	1.014	3.16
D2R13 28	1	1.85	0.520	3.56
DT9 23	1	2.04	0.770	2.64
DT11 24	1	1.98	0.772	2.57
DT14 25	1	1.94	0.70	2.79
C1R6 18	2	2.06	1.16	1.78
C1R10 19	1	1.86	0.72	2.60
C1R12 20	1	1.71	0.63	2.71
C1R16* 21	1*	1.52*	0.37*	4.12*
C1R16* 22	2*	2.11*	0.98*	2.15*
CT6** 13	1**	1.76**	0.70**	2.5**
CT6** 14	2**	2.16**	1.21**	1.79**
CT10 15	2	2.17	1.23	1.77
CT12 16	2	2.14	1.24	1.73
CT16 17	2	2.01	1.00	2.01
B1R4 10	2	1.71	0.903	1.90
B1R10 11	2	1.57	0.824	1.90
B1R14 12	2	1.44	0.70	2.1
BT4 7	2	1.59	0.91	1.75
BT10 8	2	1.50	0.81	1.85
BT14 9	2	1.45	0.74	1.96
A1R7 4	2	1.21	0.68	1.77
A1R19 5	2	1.11	0.62	1.81
A1R24 6	2	1.05	0.54	1.93
AT7 1	2	1.19	0.69	1.72
AT19 2	2	0.99	0.55	1.81
AT24 3	2	0.97	0.52	1.85

Column Code 1 = Styragel Column Packing

Column Code 2 = Bioglass column Packing (Results from Polymer Corp.)

* and ** are those samples which were analyzed with the two different columns.

APPENDIX D

Determination of Temperature Rise Inside Vials

D.1 Introduction

Styrene, like many vinyl-type compounds, polymerizes readily at elevated temperatures. Since styrene polymerization is exothermic (22), it behaves much like an autocatalytic reaction. A temperature rise accelerates the rate of polymerization which in time liberates heat and further rises the temperature. This may result in a runaway reaction with resulting high temperatures and accompanying high pressure.

The heat of polymerization of styrene is about 17.8 K cal/mole or 160 cal/gm (22), (288 Btu/lb) of monomer. This is roughly equivalent to the heat of hydrogenation of one double bond. From this a simple calculation shows that if none of the heat of polymerization were lost, it would be sufficient to raise the temperature of the polymer above 300°C. Experimentally, it is found that the temperature inside a reaction container is always higher during polymerization than the ambient temperature of the bath. This effect varies, of course, with the size of the container and the rate of polymerization. Even when a container is no larger than a vial of 18 MM outside diameter, the excess temperature can amount to 8-14°C (44) depending upon the efficiency of heat transfer to the surrounding medium.

During the early stages of polymerization the monomer is sufficiently fluid for convection to transfer much of the excess heat from the center to the walls of the container. Further polymerization increases viscosity and reduces convection so that heat dissipation must depend principally upon conduction through the polymer mass. The thermal conductivity of polystyrene is very low and hence, most of the heat of polymerization which is liberated at points more than a few millimeters from the walls of the reaction vial results in a rise in the temperature of the polymerizing mass.

For a careful kinetics study of the polymerization one has to consider this factor, because the polymerization temperature affects not only the rate of polymerization but also the molecular weight of the product. Attempts were made to avoid this important cause of misleading results in the polymerization study by choosing the reaction vials as small as possible. Also the temperature rises inside the vials were measured at different temperatures.

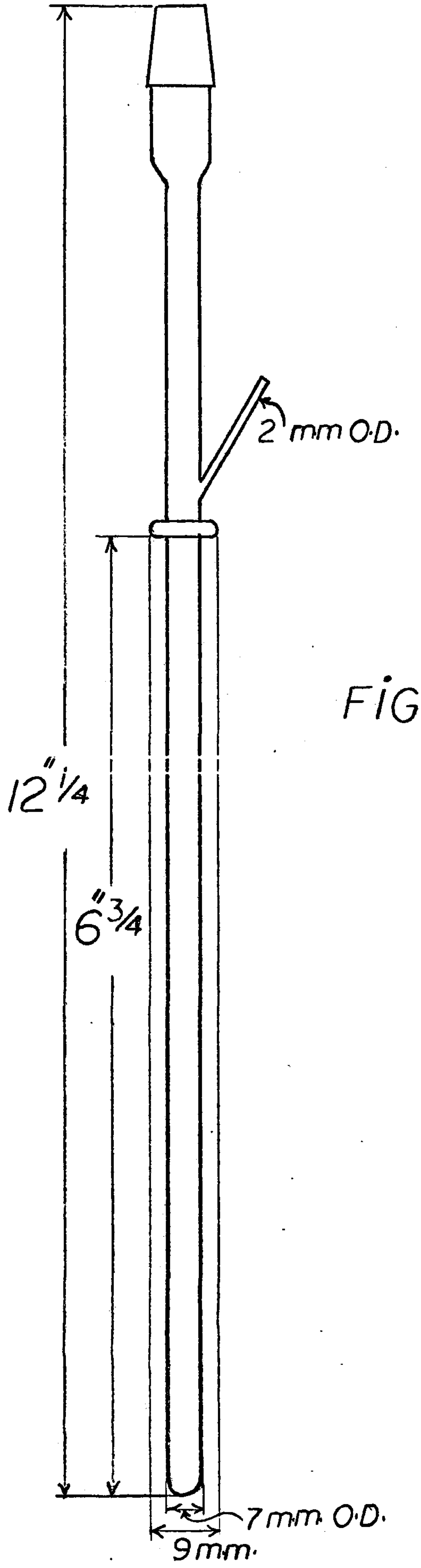
D.2 Apparatus and Procedures

D.2.1 Temperature Rise in Reaction Vials

Reaction vials of 7 MM O.D. were chosen for this investigation. They have a side connection of 2 MM O.D. capillary tube was provided. Figure D.2.1 shows more detail of the vial.

Iron-Constantan thermocouples were used for measuring the temperature inside the vial. Most of the other thermocouples are suitable for this study except copper-constantan. Experiences have shown that if styrene monomer contacts copper or copper-bearing alloys it picks up enough copper to give definite inhilitor action during subsequent polymerization (62).

VIAL WITH
SIDE CONNECTION



FIG·D-2-1

Several samples were prepared in the following manner. After cleaning the thermocouple surface it was sent through the side capillary of the vials and the top part of the capillary was sealed with special sealing resin (ceramic-glass R.T.V.).

The sample was then prepared as in section A.2 of this report, except one section of the vial was sealed (top part). The other end of the thermocouple was connected to the recorder and cold junction of the system. In order to measure the temperature inside the prepared samples the following steps were used:

1) the sealed vial was put in the ice bath and the 0°C was recorded for several minutes
2) Along with the first step the desired oil bath temperature (say 165°C) also was checked and recorded
3) The vial was dropped in the oil bath and the time of this action was recorded by a stop watch
4) The recorder pen starts to record the temperature rise inside the vials. As soon as it records the equivalent temperature with the oil bath temperature (say 165°C) the time was recorded again. The difference in time recorded shows desired time for the vial content to reach the required reaction temperature.

With the same procedure the cooling time of the polymerized samples were measured except that this time the vials were put back into the ice bath and the time required to reach 0°C was measured. This measuring also is important from the point of stopping the reactions at a certain stage.

D.3 Results and Discussion

Cooling and heating times were measured for four different temperatures. Each experiment was repeated three times and the resulted average times are shown in Table D.3.1.

TABLE D.3.1

Temperature Range °C	Average Heat-Up Time Sec.	Average Cool-Down Time Sec.	Number of Samples
0 - 160	100	38	3
0 - 165	90	42	3
0 - 180	70	48	3
0 - 200	45	52	3

It has been observed that at 200°C the temperature was still rising even after the first 45 seconds. This rise in temperature lasted for nearly 3 minutes and then it started to come down and stayed at 200°C. As can be observed from the gravimetric data in Section 7 of this report, in the first 3 minutes and 200°C styrene will polymerize up to nearly 30% conversion. This high rate of polymerization most probably is the cause for that excess of temperature over 200°C.

Obviously, this phenomenon can be observed at other temperatures but with lower temperature rise (because the rate of polymerization is lower at lower temperatures).

The excess temperature at 200°C was about 5°C. The accuracy of this temperature rise is open to objection, for several reasons. The most important of all is the trace impurities, which even to the extent of a fractional PPM, may greatly alter the behaviour of a monomer during this polymerization process.

Boundy and Boyer (62) have gathered a good deal of information on this subject. The thermocouple in the reaction vial can be counted as an impurity. For any kinetics study which needs accurate data one has to reduce the size of the vial even to a smaller diameter than 7 MM O.D., because the polymerization is a cumulative reaction and any factor which influences the start of this reaction will maintain its effect on the subsequent polymerization.