POST-IRRADIATION STUDY OF HIGHLY CONVERTED STYRENE-POLYSTYRENE SYSTEMS

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By

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"TO THE MEMORY OF A GREAT LEADER, TO NASSER"

"You've been listening at doors - and behind trees - and down chimneys - or you couldn't have known it."

"I haven't indeed" Alice said very gently. "I found it in a book."

Lewis Caroll

"Through the Looking Glass"

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SCOPE AND CONTENTS:

The post-irradiation annealing of highly converted styrene-polystyrene systems was explored. Experimental conditions necessary for the entrapment of high concentrations of free radicals in such systems were investigated. They were found to bear a relation to the glass transition temperature of the system.

The concentration of free radicals formed by subjecting the polymer-monomer systems to Gamma rays, at room temperature, was measured, and the subsequent G_M and G_P values were calculated. The structure of the formed radical was found to be in agreement with that suggested by previous investigators. The free radicals decay was examined at varied temperatures above and below T_{gs}, and was found to follow a second order mechanism. The activation energy of decay was found to increase by raising the temperature above T_{gs}.

When irradiation was executed at temperatures below T_{gs}, post-irradiation annealing led to high rates of polymerization when carried out at temperatures above T_{gs}.

The number average molecular weight was practically unchanged during the polymerization of the last few percent monomer.

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NOMENCLATURE

M_n = The number average molecular weight

M_w = The weight average molecular weight

M_z = The Z average molecular weight

M = Monomer

P = Polymer

$R^{\bullet}$ = Free radical in general

$P^{\bullet}$ = Polymer free radical

$M^{\bullet}$ = Monomer free radical

P_r = Polymer of chain length r

$G\ \bar{R}^{\bullet}$ = The G-value for free radicals production

C = Concentration

K_d = Rate constant of catalyst dissociation

$R^{\bullet}_c$ = Catalyst free radical

$R^{\bullet}_1$ = Primary radical

$R^{\bullet}_r$ = Radical of chain length r

K_i = Rate constant for the formation of primary radicals

K_p = Propagation, rate constant

K_t = Termination, rate constant

K_{tc} = Termination by combination, rate constant

K_{td} = Termination by disproportionation, rate constant

K_{tr} = Transfer, rate constant

K_{sm} = Propagation of $S^{\bullet}$, rate constant

$[M]$ = Monomer, concentration

$[P]$ = Polymer, concentration

$[R]_r$ = Free radical of chain length r, concentration

$[R]$ = Total free radical concentration

R_o = Overall polymerization rate

I = Rate of initiation

f = Catalyst efficiency

D_r = Dose rate

t = Time

T = Temperature

E = Activation energy

R = Gas constant

D = Diffusion coefficient

$G_{M\cdot}$ = G-value for monomer free radicals

$G_{P\cdot}$ = G-value for polymer free radicals

T_g = The glass transition temperature

$T_{g\infty}$ = The glass transition temperature of a polymer of infinite chain length

T_{gp} = The glass transition temperature of a pure polymer

T_{gm} = The glass transition temperature of the monomer

T_{gs} = The glass transition temperature of a polymer-monomer system

ρ = Density

N = Avogadro's number

Θ = The contribution of a chain end to the free volume

αp = The difference between the volume expansion coefficient of the polymer in melt and in a glassy state

Q_p = Volume % polymer

αm = The difference between the volume expansion coefficient of the monomer in melt and in a glassy state

Q_m = Volume fraction of the monomer

D_t = Total dose

$\frac{u}{\rho}$ = The mass energy absorption coefficient

$\left[R^{\cdot}{}_{o}\right]$ = Initial free radicals concentration, immediately following irradiation

π = Osmotic pressure

$\left[R^{\cdot}{}_{o}\right]_p$ = Initial polymer free radicals concentration immediately following irradiation

CHAPTER I

INTRODUCTION

1.1. Statement of the Problem:

It is well known that the polymerization in bulk, of the last few percent monomer in a polymer-monomer system, requires either one or a combination of the following:

(i) In the case of thermal bulk polymerization, temperature should be raised substantially to shorten the reaction time (this is known to cause chain degradation which is not desirable), or else catalyst should be used, and although this is a better approach, the catalyst is costly, and may affect the produced polymer properties in an undesirable manner.

(ii) When radiation energy is used, the marked acceleration, observed in the rate of polymerization between 40-90% conversion (H3) ceases above this range and the % conversion vs time plot tends to level off, and therefore, a relatively long irradiation period is required to bring the reaction to completion.

Higher dose rates and irradiation temperatures speed up the reaction (H3, C4) (see Fig. C & D), a lower molecular weight polymer is produced which is generally not desirable.

It is therefore, clear, that a large amount of energy (thermal, radiation, or a combination of both) is required, particularly when no catalyst is used, to bring a polymer-monomer system of a % conversion greater than 90%, to a 100% polymer in a reasonable time.

Polymerization is known to proceed via a free radical mechanism for a large number of monomers including styrene (B1, C4) (some contribution of ionic mechanism takes place at very low temperatures). It is also well known (B7) that free radicals become trapped in the solidifying polymer. Accordingly, the aim of this research was to use gamma rays to generate free radicals in a highly converted system, and to investigate the decay of free radicals together with the progress of polymerization after irradiation. A series of annealing temperatures (equal to and above ambient) was contemplated.

CHAPTER II

REVIEW OF PREVIOUS WORK

2.1. Historical Review:

2.1.1. Polystyrene and Styrene:

Prior to 1786, styrene was first discovered by Newman (B 17). He separated an "essential oil" from storax; this oil was later found to be styrene.

Most of the credit for the discovery of styrene is given in the literature to E. Simon (1839). Ref. (S12) was found to be the earliest mention of the name "styrol". Simon obtained styrene by the distillation of a "natural balsamic material - storax (liquidamber)". He noted the styrene's ability to form a jelly-like material (i.e. polymerize) after several months of storage. Bonastre (B16), eight years earlier than Simon, also obtained styrene by the distillation of balsam and described its properties. Although Simon may have the credit for naming the material, it had at least been isolated and described by Bonastre earlier. Simon believed that the solid residue obtained after several months of styrol storage was "styrol oxide".

Blyth and Hoffman (B14) in 1845 proved that this was not correct and that the solid body has the same chemical structure as styrol. They named it "meta-styrol". Blyth and Hoffman (B15) were also the first to demonstrate the depolymerization capacity of polystyrene to styrene under the influence of temperatures of 200°C and higher. In (1866), Berthelot's (B11) studies revealed the importance of catalysts in speeding up the polymerization process.

Before 1930, the monomer and the polymer were produced more or less on the lab scale. About 1930, the Dow Chemical Company started styrene manufacture; by World War II, styrene was playing a major role in the manufacture of synthetic rubber. Today, its tonnage production has reached second or third place among the synthetic aromatic organic chemicals.

Polystyrene, $(C_8H_8)_n$, is formed by directly heating the monomer; at times in the presence of a catalyst. The average molecular weight decreases with the increase of the polymerization temperature, addition of catalyst, and the presence of impurities. The value of n for commercial polymers ranges from 500-2000.

2.1.2. Styrene Polymerization:

Kronstein (K 7), made a serious attempt to analyse the process which takes place before solidification. He found that polymerization proceeded in two steps: a) thickening, followed by b) gelatinization.

Ostromislensky (O. 3) advanced some valuable ideas about the mechanism by which polymerization proceeds. Staudinger (S16) was also a dominant figure in the field of polymerization. He put forward the theory about polystyrene chemical structure, proposing that it consists of a large number of styrene monomer units connected through their vinyl groups, and suggested to call the compound "Polystyrene" rather than "Metastyrene".

For commercial purposes, polymerization of styrene in bulk proved to be superior to the suspension and emulsion methods. However, it involves the difficulty of controlling the temperature, due to the exothermic nature of the reaction.

2.2. Polystyrene, Its Properties and Uses:

The main properties of polystyrene which caused its widespread use are:

(i) Excellent moldability over wide ranges of pressure and temperature.

(ii) Extremely good dielectric properties.

(iii) Dimensional stability and rigidity.

(iv) Low moisture absorption.

(v) Easily coloured.

(vi) Odourless and tasteless.

(vii) Thermoplastic.

(viii) Low specific gravity.

(ix) Chemically inert and resistant to the corrosive effects of inorganic liquids.

(x) Above all, its low production cost makes it a very attractive investment. Ref. (B.17) provides a table containing all the physical constants of polystyrene.

Polystyrene and the styrene-based molding and extrusion plastics are used in the following applications:

(i) Packaging: small molded containers, lids and closures, bottles and jars. Foamed polystyrene as cushioning material

(ii) Appliance housings and parts, for which purposes, a little over 25% of the styrene based plastics are applied.

(iii) Engineering uses: its copolymers usually have good mechanical properties such as impact resistance. It is particularly used in automative industry such as "instrument clusters and dash panels, seat, door, and roof panels", boats, telephones, luggage, shoe heels, and pipes.

(iv) Miscellaneous: toys, houseware, wall tiles

(v) Its excellent dielectric properties makes it attractive to use in miscellaneous radios and radar accessories (coil forms, sockets for small tubes, spacers, stand-off insulators, and connectors for cables).

Its low heat distortion point has limited its application where heat is involved.

The reader is referred to Ref. (B.17) for a complete coverage of polystyrene fabrication, application, and uses.

2.3. Molecular Weights:

Polystyrene's physical properties, like any other polymer, depend on its average molecular weight, molecular weight distribution, and chain geometry.

A polystyrene sample with an average molecular weight of 10^5 i.e. approximately 10^3 monomer units/chain, may have chains consisting of 50 monomer units up to chains consisting of 2×10^4 monomer units. Macromolecules forming the polymer mass vary in their degrees of polymerization; as a result, any polymer sample is characterised by a molecular weight distribution that can be represented by a distribution curve of the type (see diagram below).

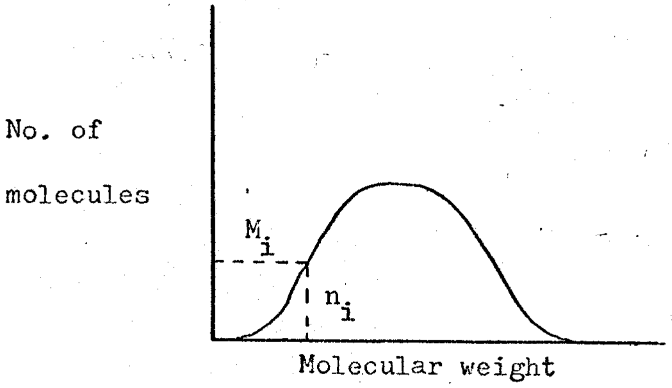


Figure 2.1.

Different methods of molecular weight averaging give several types of average molecular weights. A polymer sample containing n_1 monomer molecules each of molecular weight M_n, n_2 dimer molecules of molecular weight M_2 and... n_i molecules of molecular weight M_i etc... Therefore, according to (C12):

N_i = The fraction of molecules having the molecular weight M_i

$= n_i / \sum_i n_i$

W_i = Their weight $= n_i\ M_i$

w_i = Their weight fraction $= \frac{W_i}{\sum_i W_i}$

The number average molecular weight is the mean molecular weight obtained by counting the number of molecules:

$$M_n = \sum_i n_i M_i / \sum_i n_i = \sum_i N_i\ M_i$$

The weight average molecular weight is the mean molecular weight obtained by counting the weight of molecules with a given molecular weight:

$$M_w = \sum W_i M_i \Big/ \sum_i W_i = \sum_i w_i M_i = \sum_i n_i\ M_i^2 \Big/ \sum_i n_i\ M_i$$

The Z-average molecular weight:

$$M_z = \sum_i (W_i M_i)\ M_i \Big/ \sum_i W_i M_i = \sum_i n_i M_i^3 \Big/ \sum_i n_i M_i^2$$

The diagram given below illustrates the relative positions of M_n, M_w, and M_z on the molecular weight distribution curve

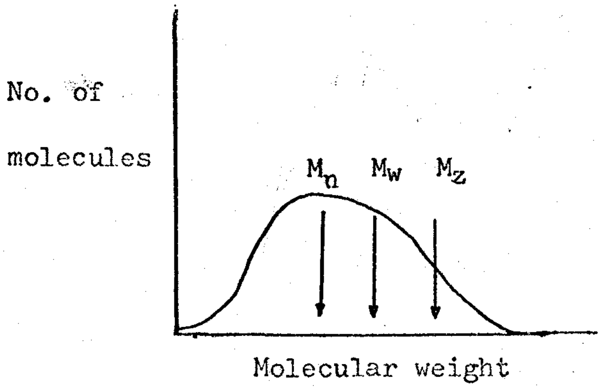


Figure 2.2.

M_w/M_n is known as the degree of despersion

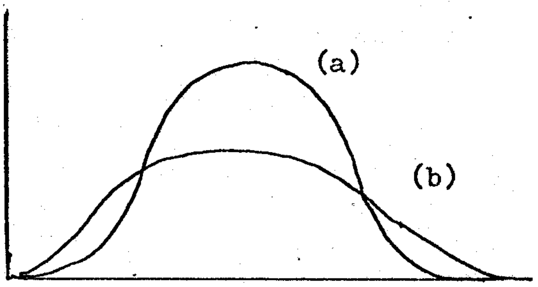


Figure 2.3.

a) Polymer with a narrow molecular weight distribution e.g.

$M_w/M_n = 1.2$

b) Polymer with a large molecular weight distribution e.g.

$M_w/M_n = 2.5$

A truly monodispersed sample gives $M_w/M_n = 1.0$. The terms: number average M_n, weight average M_w and Z average M_z molecular weights have been introduced and defined by Lansing and Kraemer (K. 6).

The most widely used technique to determine the number average molecular weight of a polymer is the osmometry technique. Light scattering is used in determining the weight average molecular weight and the Gel Permeation Chromatography provides the most rapid method for determining molecular weight distributions.

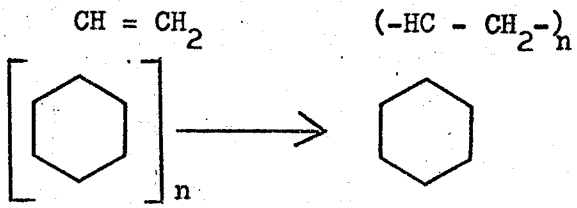
2.4. The Effect of residual monomer on the polymer properties:

The presence of any residual monomer in the polymer, greatly affects the latter's properties. For, inspite of the rapidity of polymerization at the beginning, it slows down when the solid state is reached, so that after it is about 90% complete the remaining polymerization proceeds at a very low rate (B17, H10, R.3, H.1).

Any unpolymerized monomer reduces the polymer heat distortion point and eventually produces blushing and crazing. Finally it promotes discolouration of the product at high temperatures or in the sunlight, which is due to the monomer sensitivity to oxygen. In addition, since styrene is toxic on ingestion, polymer containing any residual monomer cannot be used for food containers.

2.5. Polymerization, its nature and means:

Styrene polymerization is a chain reaction which can be accomplished by all known polymerization techniques. The reaction is represented schematically as follows:



(See P 11 & P 17-22 for details)

The exact nature of the beginning and end of such a polymer chain is not certain. This reaction proceeds by heat alone and/or with the aid of catalysts. Ionizing radiation is another source of energy by which polymerization can proceed. In bulk, the rate increases expontentially with temperature, requiring months at room temperature but only a few hours at 150°C (C.4).

The problem of polymerizing the last traces of monomer is of great importance due to the impracticality of continuing the reaction for long periods of time. On the other hand, leaving traces of monomer in the polymer will greatly harm the polymer properties as was previously mentioned. Fortunately, a brief finishing treatment at higher temperatures with the use of special polymerization catalysts is a current method of producing a low volatile content polymer.

Ultra violet spectrophotometry is a good tool for the determination of unpolymerized styrene in polystyrene, especially for the last 2% monomer.

2.6. Polymerization by Radiation:

2.6.1. Historic Background and Development:

Since World War II, the use of high energy radiation to initiate polymerization has attracted much attention. As early as 1938, Hopwood and Phillips (H.5, H.6), used γ-rays and fast neutrons to polymerize several vinyl monomers. S-shaped conversion curves were obtained. Most of the work reported in the early years of investigation is not technically valuable due to the fact that it was carried out under unsatisfactory experimental conditions (dosimetry problems, the presence of oxygen, etc...).

Magat (and his co-workers) in 1948 studied the radiation induced polymerization of some vinyl monomers with special emphasis on styrene. He studied the effects of different types of radiation on the polymerization reaction, such as γ-rays (C. 3, C. 5), X-rays (P. 5), and the mixed radiation from a nuclear reactor (C. 5, L.1).

Chapiro (C.4), provides a good literature review of the progress made in the field year after year.

The main features of radiation polymerization are basically similar to those of conventional free radical polymerization, the radiation role being merely limited to the primary events which lead to the free radicals production and to a few specific secondary effects. At high conversions, the polymer itself is radiolyzed and the polymeric free radicals thus generated, contribute to the chain initiation.

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

$$P \rightsquigarrow 2P^{\bullet} \quad (\text{or } R^{\bullet} + P^{\bullet})$$

(For more detail on the elementary reactions, see P17)

The initiation by polymer radicals $P^{\bullet}$, results in a polymer molecule of higher molecular weight than if a small radical $R^{\bullet}$ is involved.

From the considerable amount of experimental data now available, it is established that in most cases the polymerization by radiation at and above R.T., can be fully accounted for by free radical processes. However, conclusive evidence is now available for the contribution of ionic reactions in some specific systems under particular conditions (O. 2, S. 8), mainly when the reaction is at very low temperatures, or when the monomers are in the solid state (L.3). Ref. (P.3) is of the unique opinion that styrene polymerization is generally an ionic one if the monomer is very pure and dry.

2.6.2. The Nature of Radiation:

Different types of radiation possess the name "ionizing radiation". This term indicates that a certain type of radiation is capable of producing ions directly or indirectly in a medium of common elements such as air or water. This implies that the radiation energy is higher than the ionization potentials of O_2, N_2, and H_2 (i.e. 10-15 e.v.). This represents a lower limit for the term ionizing radiation. On the other hand, the upper limit reached at the present time exceeds several B.e.v. (1 Bev=10^9 e.v.).

γ and X-rays are electromagnetic waves not capable of producing ionization directly, but are capable of transferring their energy to charged particles which are themselves ejected from the absorbing molecules and create secondary ionizing tracks (C 4).

Gamma radiation main sources are cobalt 60 with a half-life of 5.3 years, and cesium 137 with a half-life of 33 years. The first is by far the most widely used as a gamma ray source due to the ease of its preparation and because the beam of gamma rays emitted is similar in penetrating power to that emitted by radium. It provides two strong gamma protons with energies of 1.17 and 1.33 M.e.v.

Ref. (S15, S18) provides a complete summary of radiation sources.

2.6.3. Radiation Yields:

The yield of a certain change as a result of the irradiation of matter depends upon:

a) the intensity of radiation

b) the number of active chemical species produced per photon of radiation.

2.6.3a. Radiation Intensity

Radiation intensity is defined as the energy flowing through unit area perpendicular to the beam per unit time. Generally, it is expressed in ergs per square centimeter second, or watts per square centimeter.

Until recent years, the amount of radiation received by a chemical substance was determined by measuring the ionization produced by the same radiation beam in air, followed by deriving the amount of energy dissipated in the irradiated medium from that released in air by using the mass absorption coefficients ratio. This is called an exposure dose and is expressed in roentgen.

On the other hand, a measure of the radiation energy actually interacting with the irradiated matter is called the absorbed dose, and is expressed in rads. The rad is defined as the unit of absorbed dose, and is 100 ergs per gram or 6.24×10^{13} electron-volts per gram or 2.78×10^{-9} watt hr/gm.

2.6.3b. The G Value

Burton (B22) introduced this term for expressing radiation-chemical yields. It is a measure of the absolute chemical yield of an irradiated system expressed as the number of individual chemical events occuring per 100 e.v. of absorbed energy. Therefore, G (c-1) is a symbol for the absolute number of cross links produced per 100 e.v. absorbed.

Similarly $G(R^{\cdot}) = \frac{\text{no. of free radicals produced}}{\text{100 e.v. of absorbed energy.}}$

In hydrocarbons, the $G(R^{\cdot})$ values fall within 0.01-10.0, the lower values for aromatic hydrocarbons and the higher values for aliphatic ones. This difference is explained as being the result of resonance energy absorption by the benzene ring which stabilizes the molecules against the breakage of a C-H bond. If a chain reaction results from radiation, the G-value of the reaction can reach a few millions.

A styrene molecule is resistant to radiation as a result of the conjugation of the vinyl double bond with the phenyl ring.

This structure results in the falling of all carbon atoms in the same plane, and owing to the delocalization of π electrons, any excess energy corresponding to an excited state will be randomly distributed over the whole molecule (C.4). It follows that only a fraction of the total energy is available for rupturing a certain bond. Therefore, the probability of free radicals production from a structure of that nature is low. Ref. (C.4) collected values for G ($R^{\cdot}$) for styrene from the literature, and plotted the logarithm of the dose rate vs G ($R^{\cdot}$) (see Fig. E).

Chapiro averaged data for G($R^{\cdot}$) for styrene to be = 0.69 radicals per 100 e.v. Data obtained at dose rates lower than 2-3 rads/sec result in values around the above given figure; however, for dose rates higher than that, the reported G($R^{\cdot}$) values fall to about 0.3. A value of 0.22 is reported by (S.7).

These values are calculated from experimental rates of polymerization with the assumption that the simplified kinetic scheme applies (see P19) to the reaction over the whole range of dose rates.

Chapiro related the observed decrease in G ($R^{\cdot}$) at high dose rates, to the fact that the simplified kinetic scheme no longer applies when the dose rate reaches a critical value. He reported that some investigators did not take that into account.

However, the result obtained in the present investigation, for G($R^{\cdot}$) of styrene monomer is = 0.215, and it applied a direct means of experimentally measuring the free radicals' concentration, rather than the uncertain kinetic method that was carried out at high dose rates.

This result, along with other results reported in the literature for polystyrene free radicals, contradicts Chapiro's explanation for the cause of the lower G($R^{\cdot}$) values obtained at high dose rates.

The molecular structure of polystyrene is less stable than styrene monomer since the polymer has less resonance stabilization. Comparison with similar systems for which experimental results are reported lead to estimating G $(R^{\bullet})$ for polystyrene to be twice or more as great as that of the styrene monomer (C.4). Later in this chapter experimental values reporting the $G(R^{\bullet})$ for polystyrene will be given.

2.6.4. Degradation and Cross Linking:

Radiation can affect polymer molecular weight in two ways. The first is by linking molecules together, therefore, increasing the molecular weight, or it can decrease it by inducing main-chain degradation.

Polystyrene is clasified as a cross linking polymer. This simply means that G(c-l) is greater than G (degradation) (in vacuum). The linking involves the benzene ring as well as the main chain, with liberation of hydrogen $G= 0.013 - 0.026$ (W.1). The ratio of degradation to cross linking which is generally accepted is 0 to 0.2.

Various methods of measuring yielded different results (C.9, S.11). Recently Ref. (K.5) introduced a direct method for determining cross linking and chain scission in polymers.

The presence of oxygen causes linking of polystyrene to be replaced by degradation (W.1). Oxygen diffusing into polystyrene after irradiation causes carbonyl and hydroxyl groups to be formed, possibly by reaction with free radicals or double bonds (S. 6 C4).

2.6.5. Free Radicals as Formed by Radiation:

Free radicals are species that possess an unpaired electron (e.g. $CH^{\bullet}_3$, $C_6 H^{\bullet}_5$, $Cl^{\bullet}$ and $N^{\bullet}a$). Species with two independent unpaired electrons, such as $\dot{C}H_2-CH_2-CH_2-CH^{\bullet}_2$ are called diradicals. They contain two essentially independent odd electrons.

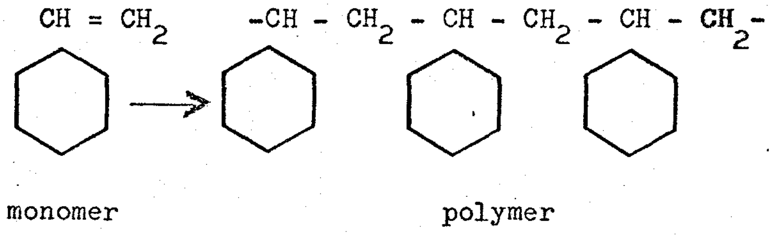
In conformity with spectrographic nomenclature, if the two electrons have parallel spins, the species is called a triplet. If they have anti parallel spins, the species is called a singlet. Triplet species are often produced in photochemical and radiolysis processes (P.6).

Little is known about the mechanism by which radiation produces chemical changes in polymers. Irradiation of polymers at or below room temperature, followed by testing samples for the presence of free radicals with the use of Electron Spin Resonance spectrometry, gave positive results. Examples can be found in Refs.(A1, A3, A6, A7, C1, F1, K.2, K.3, O.1, M.7, S.2, T2, W3).

Refs.(A3, F.1, S.2, S.1) reported the detection of free radicals in irradiated polystyrenes. The reported results are often different. Estimate yields of free radicals obtained by the Electron Spin Resonance technique will be given later in the chapter. However, the one usually accepted for polystyrene is G=0.2 (A.3). Later in the chapter there will be a return to the subject of free radicals, for a brief discussion of their methods of entrapment.

2.7. Polymerization Kinetics:

Vinyl monomers such as styrene, polymerize through an addition reaction. The polymer produced from such a reaction is a repetition unit of the monomer.



A free radical mechanism is the general case for such reactions, although under special conditions the mechanism could be an ionic one. Refs.(B21,P.2) are suggested as a good review for such mechanisms.

The other major class of polymerization reactions is the condensation one, where two molecules get together with the production of of big molecule (polymer), and a small molecule such as water, e.g. a hydroxy acid:

$$\mathrm{HO\text{-}R\text{-}COOH + HO\text{-}R\text{-}COOH \rightarrow HO\text{-}R\text{-}COO\text{-}R\text{-}COOH} + H_2O$$

dimer

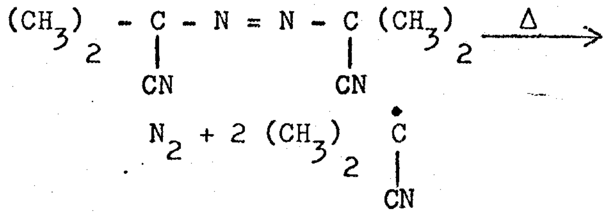
$$\mathrm{HO\text{-}R\text{-}COOR\text{-}COOH + HO\text{-}R\text{-}COOH \rightarrow HO\text{-}R\text{-}COO\text{-}R\text{-}COO\text{-}R\text{-}COOH} + H_2O \text{ etc...}$$

trimer

This type of reaction however, is not relevant to this investigation. Ref. (B21) can provide the reader with adequate information on the subject.

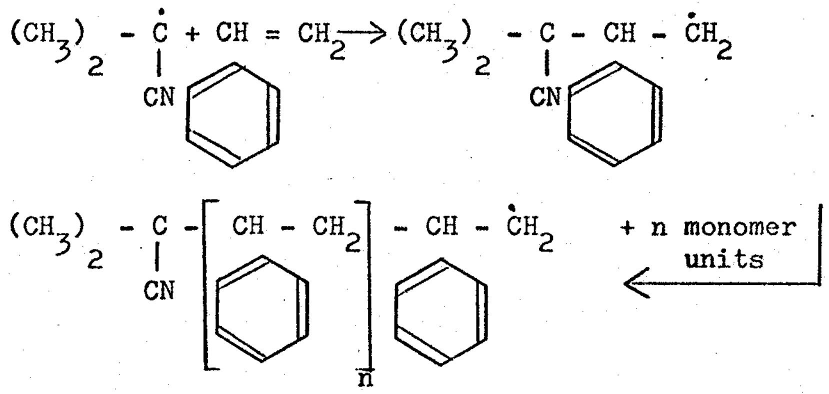
The first step in the free radical polymerization is the initiation one. The reaction can be induced by heat or radiation, with or without the presence of a catalyst. The presence of a catalyst facilitates the understanding of the initiation step.

e.g. Azobisiobutyronitrile



$$(CH_3)_2-\underset{\mathrm{CN}}{\underset{|}{C}}-N=N-\underset{\mathrm{CN}}{\underset{|}{C}}(CH_3)_2 \xrightarrow{\Delta} N_2 + 2\,(CH_3)_2\underset{\mathrm{CN}}{\underset{|}{\dot{C}}}$$

The produced catalyst free radical reacts with the monomer, producing a new radical capable of propagating with other monomer units to form long chain free radicals:



The use of a catalyst, somewhat complicates the kinetics of polymerization due to its consumption during the reaction. It follows that the catalyst effeciency is apparently changing, thus causing the rate of free radical production to vary along the progress of polymerization:

$$- \frac{dc}{dt} = k_d c$$

where c is the catalyst concentration.

The use of radiation alone, eliminates such a source of complexity, but on the other hand introduces others, such as the initiation by polymeric radicals (C.4).

When thermal or radiation energy is used alone, the first product might be a mono or a diradical. Several investigators support each theory with a greater tendency towards the diradical. Refs.(F.2,H.8) support the thermal diradical theory and Refs.(B.3,M2, M3) support the radiolysis diradical one. Ref. (B 21) is a good review for all theories put together.

The kinetic scheme of both catalytic and radiation polymerization are very similar. The main difference is caused by the non discriminatory nature of radiation. This leads to the breaking of any intermolecular bond to generate free radicals. Consequently, monomer, polymer, or even solvent molecules (if present) can produce free radicals under the effect of radiation. The initiation reaction can be represented for radiation polymerization by:

$$M \rightsquigarrow R^{\bullet} \qquad 2.1.$$

and for a catalyst initiated reaction:

$$C \xrightarrow{K_d} 2R^{\bullet}_{c} \qquad 2.1a.$$

$$R^{\bullet}_{c} + M \xrightarrow{K_i} R^{\bullet}_{1} \qquad 2.1b.$$

This reaction as applied to azobisisobutyronitrile and styrene monomer has been previously given in detail on (P18).

<u>Propagation</u>:

$$R^{\bullet}_{1} + M \xrightarrow{K_p} RM^{\bullet} \text{ or } R^{\bullet}_{2} \qquad 2.2.$$

$$R^{\bullet}_{r} + M \xrightarrow{K_{pr}} R^{\bullet}_{r+1} \qquad 2.3.$$

This reaction proceeds until the long chain radical collides with another one, causing the termination of both.

<u>Termination:</u>

a) By combination $R^{\bullet}_{r} + R^{\bullet}_{s} \xrightarrow{K_{tc}} P_{r+s}$ 2.4.

b) By disproportionation

$$R^{\bullet}_{r} + R^{\bullet}_{ts} \xrightarrow{K_{td}} P_{r} + P_{s} \qquad 2.5.$$

In the latter, the transfer of a hydrogen atom from one radical to another terminates both, but causes one of them to acquire a double bond.

<u>Transfer</u>:

Active centres may be transferred from an active molecule to an inactive one, following their collision. This usually causes a growing chain to be terminated, but the newly formed radical may start propagating on its own, therefore, the overall reaction rate is not affected, neither is the total free radicals concentration, but chain transfer necessarily lowers the average molecular weight:

$$R^{\bullet}_{r} + SX \xrightarrow{K_{tr}} R_{r}X + S^{\bullet} \qquad 2.6.$$

$$S^{\bullet} + M \xrightarrow{K_{sm}} R^{\bullet}_{1} \qquad 2.7.$$

Where SX could be a monomer, or any added substance (such as a solvent), and X is the most labile atom (usually H or Cl)(C.4).

In order to determine the reaction rates, simplifying assumptions have been introduced, and can be found in most polymerization kinetics monographs such as (B.1, B21).

The first assumption is that the propagation rate constant is independent of the propagating radicals chain lengths:

$$K_{p1} = K_{p2} = ---------- = K_{p}$$

This is also assumed to apply to:

$$K_{tc} \quad K_{td} \quad \text{and} \quad K_{tr}$$

The second assumption is to neglect the monomer consumption in reactions other than the propagation one, i.e. from equation (2.3.)

$$-\frac{d[M]}{dt} = K_{p} \left[R^{\bullet}_{r}\right]\left[M\right]$$

therefore, for all chain lengths:

$$= K_{p}\left[R^{\bullet}\right]\left[M\right]$$

$\left[R^{\bullet}\right]$ represents the summation of all free radicals of different chain lengths:

$$= \sum_{r=1}^{\infty} \left[R^{\bullet}_{r}\right]$$

Consequently, the change in $R^{\bullet}_{1}$ concentration with time would be:

$$\begin{aligned}\frac{d\left[R^{\bullet}_{1}\right]}{dt} = I &- K_{p}\left[R^{\bullet}_{1}\right]\left[M\right]\\ &- K_{tc}\left[R^{\bullet}_{1}\right]\left[R^{\bullet}\right]\\ &- K_{td}\left[R^{\bullet}_{1}\right]\left[R^{\bullet}\right]\\ &- K_{tr}\left[R^{\bullet}_{1}\right]\left[M\right]\\ &+ K_{sm}\left[S^{\bullet}\right]\left[M\right]\end{aligned}$$

I is the rate of $R^{\bullet}_{1}$ formation. The rate of change for longer free radicals:

$$\begin{aligned}\frac{d\left[R^{\bullet}_{r}\right]}{dt} = {} & K_{p}\left[R^{\bullet}_{r-1}\right]\left[M\right] - K_{p}\left[R^{\bullet}_{r}\right]\left[M\right]\\ & - K_{tc}\left[R^{\bullet}_{r}\right]\left[R^{\bullet}\right] - K_{td}\left[R^{\bullet}_{r}\right]\left[R^{\bullet}\right]\\ & - K_{tr}\left[R^{\bullet}_{r}\right]\left[M\right]\end{aligned}$$

The final assumption is that the free radical concentration reaches a steady state in a very short time:

$$\frac{d\left[R^{\bullet}\right]}{dt} = 0$$

Therefore, the rate of initiation (I) = the rate of termination:

$$I = K_{t}\left[R^{\bullet}\right]^{2} \qquad 2.8.$$

The rate of initiation by radiation:

$$I = \phi_{M}\, D_{r}\left[M\right] \qquad 2.9.$$

Where $\phi_{M}\left[M\right]$ is the free radical production rate in the monomer expressed in moles/litre/rad, and D_r is the dose rate (D_r is relatively constant, varying only slightly due to the gradual diminishing in the radiation source's strength). On the other hand, when initiation is by a catalyst, and C_o is the initial catalyst concentration:

$$C = C_{o} \exp -\left[K_{d}\, t\right] \qquad 2.10.$$

considering that not all catalyst free radicals succeed in propagating a growing chain, an efficiency factor (f) could be introduced to relate I to

C (see P.):

$$I = 2f\ K_d\ C = 2f\ K_d\ C_o \exp -\left[K_d\ t\right] \qquad 2.11.$$

and using the second assumption, the overall reaction rate = the monomer consumption during propagation only:

$$\begin{aligned} R &= K_p\ \left[R^{\cdot}\right]\ \left[M\right] \\ &= K_p\ \ K_t^{-\frac{1}{2}}\ \ I^{\frac{1}{2}}\ \left[M\right] \qquad 2.12. \end{aligned}$$

Where I could be represented by (2.9.) for radiation kinetics and by (2.11.) for the catalyzed one. Equation (2.12.) is the classical free radical kinetic equation illustrating that the overall rate is proportional to the square root of the initiation rate. In cases of gamma initiation accordingly, the overall rate is proportional to the square root of the dose rate. The overall rate equation is:

$$R = K_p\ \ K_t^{-\frac{1}{2}}\ \left(\ \phi_m\ \left[M\right]\ D_r\ \right)^{\frac{1}{2}}\left[M\right] \qquad 2.12a.$$

Deviations from this relation were first reported by Refs. (C.6, C.8) during their radiation studies on the styrene polymerization for a dose rate range 0.006 - 7.3 rads/sec. They found that the dose rate exponent in equation (2.12.) is less than half at the highest dose rates used in their investigation. This is interpreted to be due to high initiation rates causing some of the produced radicals not to convert rapidly to growing chains i.e. the monomer units do not catch all formed free radicals, causing them to recombine without initiating polymer chains.

Very recently, Huang and co-workers (H.9) published results for the radiation induced free radical polymerization of styrene over the temperature range -0.3 to 49.5°C and at radiation intensities 9.5×10^4, 3.1×10^5, 4.0×10^5, and 1.0×10^6 rad/hr., and came to the result that the overall polymerization rate is proportional to the 0.44 - 0.49 power of radiation intensity, and that G_R.(styrene) is 0.5 - 0.8. On the other hand, Refs. (H. 3) investigated polymerization of styrene over the entire conversion range, but provided a kinetic analysis of the linear portion of the sigmoidal curves only (see Fig.C & D). Temperatures investigated are: 50°C, 70°C, 85°C, 95°C, 109°C, and at dose rates of 178, 58, and 24 rads/sec. for each temperature. Although these are higher than the dose rates used by Chapiro, no decrease in the dose rate exponent was observed for temperatures 50°C and 70°C. But at higher temperatures, the dose rate exponent was found to be 0.25 and 0.12 at 85°C and 95°C respectively. At 109°C, the dose rate exponent was found to be zero. This was attributed to an early setting of the gel effect.

At high rates of initiation, the simplified kinetic scheme given on the previous pages does not apply, and a more detailed one that takes into account mutual reactions involving free radical intermediates must be used. The reader is referred to Ref. (C.4) for details of the complete kinetics.

2.8. Polymerization at Higher Conversion Regions:

As polymerization progresses, deviation from the conventional kinetic scheme starts to occur. At conversions ranging from 10-30% (B.7) a sudden increase in both the overall polymerization rate and the molecular weight, takes place. Ref. (M.1) reported that the polymerization of several monomers in the liquid state is accelerated when it reaches a certain conversion. Trommsdorff (T.5) attributed this behaviour to a decrease in the termination rate constant K_t which becomes diffusion controlled as the viscosity of the system increases. This was later confirmed by Matheson et al. (M.4). This behaviour is generally known as the Gel-effect or the Trommsdorff effect. Styrene was reported not to show this behaviour if thermally polymerized. Ref. (B.2) attributed styrene's behaviour to a very small termination rate constant K_t which is not much affected by the viscosity increase. Accordingly, Ref. (W.2) concluded that K_t could not be diffusion controlled for styrene. On the other hand, Ref. (R.2) indicated the presence of a Gel-effect during polystyrene polymerization.

Medvedev et al. (M.6) were the first to develop the view that trapping free radicals in viscous media renders them unreactive. Investigators tried to correlate the diffusion rates to the decrease in the K_t value (R.4, V.1). Rabinowitch equation for a rate constant of a second order reaction was used for that purpose (R.1).

$$K = \frac{n\nu \exp(-E/RT)}{N_o\left[1 + \dfrac{a^2 Y \nu \exp(-E/RT)}{2(D_1 + D_2)}\right]}$$

E = activation energy of reaction

ν = frequency factor

a = shortest distance between two lattice points

n = coordination number of lattice

N_o = number of lattice points

Y = constant

T = absolute temperature

R = gas constant

D_1 & D_2 = diffusion coefficients of the two reacting particles

and since a, N_o and n are constants, the equation can be written as:

$$K = \frac{A \exp(-E/RT)}{1 + [B \exp(-E/RT) / (D_1 + D_2)]}$$

where A and B are constants.

When the diffusion of the polymer chains is unhindered, the equation simplifies to:

$$K = A \exp(-E/RT)$$

i.e. the classical Arrhenius equation. On the other hand, if D_1 and D_2, are very small with respect to B exp (-E/RT), the equation reduces to:

$$K = A (D_1 + D_2) / B$$

i.e. When a critical viscosity is reached the reaction becomes diffusion controlled.

Applying the Rabinowitch equation to polymer systems is sometimes criticised. The reason is the assumption used in its derivation "the two diffusing particles are identical with the solvent molecules". Therefore, applying it to long chain molecules is not very favourable. However, in good solvents as the monomer (such as in the case of styrene) Ref. (K. 8) justifies its use.

Vaughan (V.1) polymerized styrene thermally at 125°C, and found that the termination and the propagation reactions become diffusion controlled, with a possibility of the transfer reaction behaving in the same manner at higher percentage conversions. Spencer and Williams (S14) polymerized styrene at 125°C; the molecular weight was about 360,000. The termination and propagation reactions started to be diffusion controlled at 28% and 64% respectively. For styrene, Matheson et al.(M.4) reported a 40% acceleration of the overall rate at 44% conversion and 50°C. Fuji (F7) polymerized styrene photochemically at 25°C up to a 70% conversion and reported an acceleration of 5.2 fold and 16.9 fold at 38% and 60% conversion, respectively. He assumed that the rate constants of the individual reactions are independent of both chain length and valence character of the radical (i.e. mono or diradical). He also assumed that K_p and K_{tr} are independent of conversion. Using the equation:

$$E_a = E_p - \frac{1}{n}\left(E_t + R\,\frac{\delta(\ln q)}{\delta(1/T)}\right)$$

where:

E_a = overall activation energy of the reaction

E_p = activation energy of the propagation reaction

E_t = activation energy of the termination reaction

n = order of the termination reaction

R = concentration of the kinetic chains

T = the absolute temperature

q = the quantum efficiency of production of kinetic chains

Fuji found that E_a first decreases as the order of the chain termination n decreases. n was found to be 2 at 40% at 25°C, and 1.5 at 68%, meaning that a fraction of free radicals become inactive due to a monomolecular termination (self termination). This type of termination, apparently involves an occlusion of the chain end in regions where it is sterically inaccessible i.e. it becomes shielded by the coiling of the molecule. Shielding decreases by:

a) thermal disturbance

b) molecular weight decrease

c) the addition of chain transfer substances

Accordingly, at relatively high temperatures, no change in K_t or the termination reaction order is expected to occur.

Chapiro (C.4) pointed out that the K_t decrease causes:

a) an increase in the kinetic chain's life

b) after effects may arise

c) with the decline in the rate of termination and with the initiation rate practically constant, the concentration of free radicals increases.

As a result, the classical stationary state treatment does not apply to the kinetics. This leads to tremendous difficulties in solving the elementary differential equations. Furthermore, the various rate constants become a function of conversion. This explains the reason for the lack of a complete quantitative treatment of the Gel effect. Ref. (N.3) indicates that for several monomers K_t is inversily proportional to the medium's viscosity even at very low conversions. The critical conversion is a function of dose rate and reaction temperature (L.1).

For styrene, according to Chapiro (C.4), the Gel effect sets if polymerization is by radiolysis only. He attributed the effect to the radiolysis of the polymer molecules leading to an increase in the rate of initiation as a result of G_p being greater than G_M:

$$I = \left[G_M \cdot [M] + G_p \cdot [P] \right] \cdot D_r$$

The effect of temperature is very complex at high conversion regions. Generally, as the temperature increases, the mobility and accessibility to the growing chains increases. If termination is rate controlling, the overall rate decreases. If however, propagation is the controlling step, temperature increase leads to a very rapid overall rate. This is pronounced when the system is near the glass transition temperature, or if it contains a high concentration of trapped radicals (B.4).

According to several authors, the decrease in K_p relative to K_t occurs at higher conversions for all monomers due to the fact that E_p is greater than E_t (B8, B9, B16). Robertson (R.4), in her studies, suggested that K_p decreases at about 50%.

Schneider et al. (S.3) were the first to use the Electron Spin Resonance for free radicals studies. Ohnishi and Nitta (O.1) found that the decay of radicals produced in PMMA by gamma radiation followed a second order mechanism with K_t = 0.1 l/mole sec.

Benson and North (B10) advanced a theory for the diffusion controlled termination mechanism. They suggested a two step process: First, two polymer chain radicals diffuse together to form a proximate pair; once this has been formed, the two chains may diffuse apart without termination, or termination may occur making the second step for their suggested mechanism:

$$A + B \underset{K_2}{\overset{K_1}{\rightleftarrows}} A\cdots\cdots B \qquad 2.13.$$

$$A \cdots\cdots B \xrightarrow{K_3} AB \qquad 2.14.$$

Step (2.13.) represents a translational diffusion of the chain centres. Step (2.14.) represents a segmental diffusion of the active ends to within termination distance.

They came to the conclusion that step (2.14.) is always rate controlling.

Dole and Keeling (D.3) and Dole et al. (D.4) have cited evidence indicating that trapped radicals migrate along the polymer chain before they mutually terminate each other.

At very high % conversion chains become heavily interwined with the result that the diffusion of polymer molecules as a whole, no longer contributes significantly to the collision frequency of radicals with each other, and radical diffusion will depend on configurational changes of relatively short portions of chain molecules. Schulz (S. 4) confirmed this view. The Brownian motion of chain segments is independent of chain lengths and can take place even in a medium of infinite viscosity.

2.9. The Glass Transition Temperatures

When a liquid or a rubbery polymer is cooled there exists a narrow temperature interval known as the glass transition temperature (T_g), wherein the properties of the sample undergo a profound change to a hard glass solid. Polystyrene is a linear thermoplastic polymer, the commercial product being atactic and therefore, amorphous. The glass transition temperature (T_g) is associated with the amorphous phase of polymers. The (T_g) is perhaps the most important parameter of an amorphous polymer (T.4). An amorphous linear polymer is like a bowl of cooked spaghetti which is at a constant wriggling motion, especially at high temperatures. This segmental motion takes place in the void space offered by the free volume in the polymeric mass. Ref. (F4, W6) found that $\frac{Vf}{V} = 0.025$ at T_g for all amorphous polymers to the first approximation. Where:

V = molar volume

V_f = the free volume = $v - v_s$

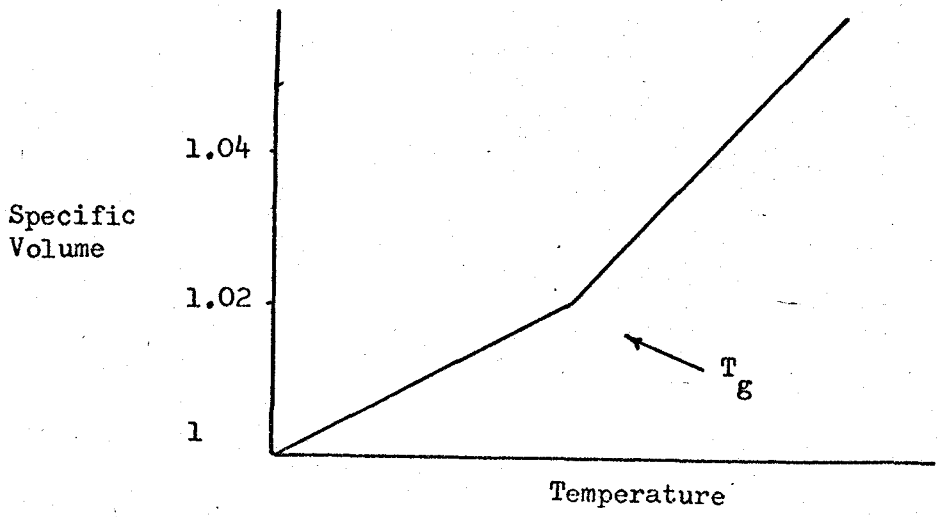
v = specific volume

v_s = volume/gm of the solidly packed polymer

By lowering the temperature, the free volume shrinks, and the thermal energy becomes small compared to the potential energy barriers for rotational and translational jumps of the polymer segment. The T_g is generally attributed to the ability of groups of atoms in the polymer chain to undergo co-operative localised motion by overcoming a thermal energy barrier. Below the T_g, thermal energy is not available to allow segments of the chain to move as a whole. Once T_g is exceeded, the motion of the segments result in a rubbery molecule.

T_g is sometimes called the internal melting point, or the softening point of the polymer. For completely crystalline materials, melting point T_m can be easily observed. But since the material becomes completely crystalline below T_m, there is no chance to observe a T_g as the crystallized material is further cooled (B20). Since polymers contain sizeable portions of amorphous material, they will give evidence of both T_g and T_m. Many properties change by passing the T_g. From a classical point of view the restriction-freedom of motion change is associated with a volume change (see Fig.2.4 below) (B 13).

Fig. 2.4.



The measure of specific volume vs. temperature is the most usual method for T_g determination. Other methods of observing the T_g involve detecting changes in the following properties with temperature: heat capacity, thermal expansion, stiffness, brittle point, tensile strength, and others.

2.9.1. Important Parameters Affecting T_g:

2.9.1a. The Solubility Parameter (δ):

The cohesive energy density is used to describe the interaction between segments of polymer molecules. It is defined as the molar energy of vaporization divided by the molar volume:

$$CED = E\,vap/V$$

The solubility parameter (δ) is equal to:

$$\delta = (CED)^{\frac{1}{2}} = (E\,vap/V)^{\frac{1}{2}}$$

T_g increases with δ. An experimental method to determine (δ) is given in Ref. (T.4). δ for polystyrene = 8.56.

2.9.1b. The Energy Barrier impeding rotation around the bonds in the chain (V_o):

As V_o increases, the internal chain mobility decreases (T.4).

2.9.1c. The Geometric Chain Stiffness:

T_g increases with the increase of the geometric chain stiffness.

2.9.1d. The Chain Length π:

The glass transition temperature depends on the chain length π in the following way:

$$T_g = T_{g\infty} - c/\pi$$

c = a constant for each polymer

$T_{g\infty}$ = the limiting value for T_g at infinite chain length

It was observed experimentally that:

$$c/\pi \longrightarrow \text{zero when } \pi \longrightarrow 500 \text{ or more.}$$

i.e. $T_g = T_{g\infty}$ for values of π equal to or greater than 500 (T. 4). It is interesting to note that for crystalline polymers:

$T_g / T_m - 0.5$	For symmetrical polymers such as polymethylene.
$T_g / T_m - 0.67$	For unsymmetrical polymers such as polytrifluorochloroethylene or isotactic polypropylene.

In general $0.5\ T_m < T_g < 0.67\ T_m$ (in °K) where T_m is the melting point. Ref. (B17,B.6, F3) found T_g for polystyrene to be = 100°C

Numerous investigators had put forward mathematical models relating the glass transition temperatures to the molecular weight-viscosity relationships. Ewart (E1) found that the relation:

$$\text{Log } M_v = (\text{Log } \eta + 4.013) / 0.74$$

(where: η = intrinsic viscosity & $\bar{M} > 3 \times 10^4$,) holds for polystyrene over the molecular weight range of 5×10^4 to 8×10^5. This result was confirmed by Ref. (K) for molecular weights 3×10^4 to 1×10^6. Pepper (P.1) worked on polystyrene in benzene at 25°C for molecular weights ranging from 800 to 11,000. The following equation represents his results for $\bar{M} < 3 \times 10^4$:

$$\text{Log } M_v = (\text{Log } \eta + 3.38) / 0.60$$

This equation has been confirmed and successfully used by Fox and Flory (F.4). According to Fox and Flory the effect of molecular weight of a polymer ($\bar{M}$) on its glass transition temperature (T_{gp}) can be represented by: (F3)

$$T_{gp} = T_{g\infty} - 2\rho N\theta / (\alpha_p M)$$

Where:

ρ = density of polymer

N = Avogadro's number

θ = the contribution of a chain end to the free volume

α_p = the difference between the volume expansion coefficients of the polymer in melt and in a glassy state

This relation was successfully applied (H.7) to methyl methacrylate and styrene. For polystyrene it becomes:

$$T_{gp} = 373 - K/M$$

K is a constant whose reported value ranges from (10^5 to 1.7×10^5) (F.3, F4, F.5), depending on the range of molecular weight for which it can apply.

2.9.1e. The Polymer to Monomer Ratio:

The glass transition temperature of a polymer-diluent (T_{gs}), depends upon the volume percentage of the polymer.

Kelley and Bueche (K.4) derived T_{gs} on the basis of the free volume theory, by assuming the additivity of the free volumes of each constituent.

$$T_{gs} = \frac{4.8 \times 10^{-4}\, Q_p\, T_{gp} + \alpha_m\, (1-Q_p)\, T_{gm}}{4.8 \times 10^{-4}\, Q_p + \alpha_m\, (1-Q_p)}$$

Q_m = volume fraction of the monomer

Q_p = volume fraction of the polymer

T_{gp} = the glass transition temperature of the polymer

T_{gm} = the glass transition temperature of the monomer

α_m = the difference between the volume coefficient of expansion in the melt and in the glassy state for the monomer

This relation was successfully used by Ref (H.7) for studying the diffusion controlled polymerization of methyl methacrylate, and styrene. They found that T_{gs} corresponds to the limiting conversion in methyl methacrylate. However, in the present investigation, (see Chap.VI), apparently no relation was found to exist between T_{gs} and the limiting conversion.

2.10. Free Radicals, their Formation, Trapping and Detection:

Definition: Free radicals are species that possess one or more unpaired electrons.

The history of radical trapping goes back about three decades. Most texts published in the early 1930's stated that free radicals are non-existent. Much earlier than that, in the 18th and 19th centuries, the term radical was used by Gay - Lussac, Leibig, Berzelius, Bunsen, and others to indicate either a combined portion of a molecule or a "free" radical. For about 130 years, attempts have been made to reach a concrete conclusion about free radicals' existence. See (P6 and B7) for details.

Lewis (L5) and his students were the first to study the production, trapping and stabilization of free radicals at low temperatures in rigid media. Subsequently, Spectrophotometry and Electron Spin Resonance were used to study free radicals entrapped in glasses.

From 1930 to 1950, free radical's studies showed that they combine with very little or no activation energies (S17), therefore, preserving them in 100% concentration could be done only near, or at, absolute zero temperature. The other alternate is to dilute the radicals with molecules that form a rigid structure. Consequently, an easy way to produce stable radicals is by freezing the material and either expose it to electromagnetic radiation, or bombard it with particles as electrons, protons, or neutrons. Free radicals can also be trapped from the gas phase by freezing the stream at very low temperatures. The easiest way for their formation in the gas phase is by heating or by an electric discharge.

The E.S.R., is a powerful tool for studying frozen free radicals. In many cases, information about their structure could also be obtained. Physical methods of free radicals' studies are much more promising than the chemical ones. In addition to the E.S.R. technique, other methods such as:

a) absorption spectra: visible, near ultra violet, infrared, or ultra violet
b) mass spectrometry
c) low temperature X-ray studies
d) low temperature emission spectra
e) magnetic susceptibility measurement
f) refractive index
g) calorimetry
h) dielectric constant measurement
i) thermal conductivity measurement

are also being used.

The E.S.R., is the most selective and most sensitive for singling out free radicals. It has the unique advantage of fair concentration determination. Its main disadvantage is the centering of all E.S.R. spectra at about one location "$g = 2$" causing superposition of spectra. The recording of the spectra as the first derivative of absorption is not very convenient either. (See section 3.6.2. for basic principles of E.S.R. theory).

Infrared methods are best used to yield information concerning details of the processes accompanying free radicals' production. The major methods of free radicals' production in the solid phase are:

1) electron bombardment
2) photolysis
3) X- or γ-rays radiolysis

The reader is referred to Ref. (B.7) for detailed information.

Statistical analysis of the limiting free radical concentration was attempted by Refs. (G1, J1), and it could be concluded that 10-14% of the matrix is the highest limit for free radicals to be successfully entrapped. However, these studies assumed free radicals to have spherical shape, which is far from being the case for polymers.

At liquid nitrogen temperature, most organic radicals possess very long life times that could be measured in years. In materials that are solid e.g. plastics, cellulose, sugars, and paraffins; radicals can be detected after storage for periods ranging from hours to months (B.7).

The change in chemical properties under the effect of radiation represents a good means of distinguishing between organic and inorganic compounds. The reactions in organic compounds are generally irreversible e.g.:hydrogen evolution during irradiation, degradation, polymerization etc...

Sisman and Bopp (S13), classified materials according to their resistance to radiation.

i) mostly elastomers which show a large decrease in strength for exposures of 10^8 to 10^9 rads.

ii) materials appreciably affected by 10^9 to 10^{10} rads. include nonrigid and some moderately rigid plastics

iii) materials showing good stability up to 10^{10} rads. mostly highly rigid plastics

Polystyrene belongs to the third class.

2.11. Activation Energies, below and above transition points:

Activation energies are usually obtained from the slope of the line in Arrhenius' plot. Discontinuity of the line is often observed. This is usually attributed to a phase change or a change in mechanism. Since a change in the physical state of the matter accompanies T_g, it is not surprising to find that numerous investigators reported discontinuity in the Arhenius plot as applied to varied systems. Ref. (C14) gives a complete coverage of the relevant literature.

According to Ref (C14), molecules equal to or larger than the monomer unit require, for their diffusion, a co-operative movement by the micro-Brownian motion of several monomer units i.e. the so called polymer segment, to take place. Below T_g, other transitions may occur, produced by the motion of short sections of the main chain or of branches. The T_g is the transition of highest temperature, and is the one most pronounced (α transition). Other transitions may be denoted β, γ, etc... in order of temperature decrease (although this nomenclature is not always observed).

Deutsch et al. (Ref. D2), used dielectric and dynamic mechanical properties measurements to obtain values for the activation energies of α and β transitions for PMMA and PMCA. Powles (P.4) used the NMR technique to obtain energies for the two transitions for PMMA. Ref (O.1) obtained a value for the α transition of PMMA by Electron Spin Resonance studies of the decay reaction of free radicals. Table (2.1.) sums up the results for PMMA

2.1.

E_α Above T_g	E_β Below T_g	Method of measurement	Reference
80		values of tensile modules	D.2
	20	dielectric	D.2
	18	aud. freq. vibr.	D.2
27 ± 10		N M R	P.4
	18 ± 4	N M R	P.4
	28	E S R	O.1

The higher values of E_α over E_β implies a larger moving entity. The β transition is assigned to the motion of the carboxy methoxy groups, while the α transition is assigned to the motion of chain segments.

Ref. (C .7) who studied the radiation initiated polymerization of MMA in dilute solutions in mineral oil at temperatures ranging (-63°C to -196°C) found that Arhenius plot for the polymerization rate showed a break at (-106°C) which was interpreted as the glass transition temperature of methyl methacrylate monomer.

When styrene monomer was irradiated in the solid state, the activation energy of the polymerization reaction was found to be -1.2 K cal/mole, by moving up to higher temperatures a change in E occurs at -18°C and becomes equal to 8.5 K cal/mole. The change in E was attributed to a change in the mechanism of polymerization, being predominantly ionic at temperatures below -18°C and changes to a mainly free radical one at temperatures above -18°C; at -18°C both mechanisms contribute equally (C.3). Ref. (C.2) investigated the effect of change of phase on the rate of polymerization by radiation, and obtained for styrene a discontinuity in the Arhenius plot with the activation energy increasing by 2-4 K cal/mole in passing the transition point.

Nara et al. (N.1) irradiated polypropylene in vacuum with gamma rays at (-196°C). The values of activation energy of free radicals decay at two temperature regions (T_A) and (T_B) were 11 K cal/mole and 48 K cal/mole respectively, which were found to be close to the values obtained for molecular motions by mechanical studies at those two temperature regions: 13 K cal/mole and 58 K cal/mole, (they represent the γ and β transition in this polymer). The latter being that associated with T_g. Nara et al. (N2) conducted a similar study on polyethylene a year later, and obtained for the activation energies of free radicals' decay reactions the following values:

Table 2.2.

Temperature region	T_A	T_L	T_B
High density polyethylene	0.4	9.4	18.4
Low density polyethylene	0.7	23.1	24.8

Ref. (S.9) used the N.M.R. technique to study the transition behaviour in polystyrene-diluents systems through distortion of absorption lines in transition regions. They suggested the existance of two major mechanisms in the course of liberation of the segmental motion in the transition region. Ref. (T1) studied the change of activation energy of polymerization at the monomer transition point under the effect of pressure and found a tremendous increase at this temperature and higher.

2.12. Free Radicals Decay:

In polymer research, so far, the creation of trapped radicals by irradiation to study their decay, structure, and after effect, was carried along either one of the two following patterns:

a) Irradiation of a 100% polymer under such conditions that the formed free radicals are stable for long periods of time. This was usually achieved by irradiating in vacuum at reasonably low temperatures. Free radicals decay studies were performed by post-irradiation annealing at higher temperatures. The Electron Spin Resonance is a common technique to follow free radicals decay. (See basic principles of E.S.R., section 3.6.2.)

b) Similarly, free radicals were created by irradiating 100% monomers in the solid state (at very low temperatures). When this was followed by higher temperatures annealing outside the radiation field; fast polymerization rates were generally observed, together with free radicals decay.

2.12.1. Free Radical Decay in irradiated polymers:

In the Electron Spin Resonance technique, the free radicals concentration is proportional to the area under the absorption curve. This area can be computed by double integrating the area under the first derivative curve obtained from the E.S.R. spectrometer.

Ref. (F. 1) found that the free radicals population in polystyrene irradiated at room temperature seemed to decay only moderately, if at all, in two weeks at R.T., but decreased by 30% after 15 minutes at 75-80°C. The initial concentration from irradiation at 298°K was less than that from irradiation at 77°K. In the absence of growth and decay curves, it can not be asserted whether the low yield at 298°K indicates a low initial yield or concurrent production and decay. Ref. (A3) irradiated polystyrene, with gamma rays, at R.T. in vacuum. The spectrum obtained was reported unchanged for several months.

Kampbell et al. (K.3) found that γ irradiation of polyethylene terphthalate (50% crystalline) at (-196°C) in vacuum, produces free radicals for which the yield is proportional to the total dose within the range (0-20 M rad), and is independent of the irradiation temperature within the range (-196°C to 25°C). For a dose rate of 0.2 M rad/hr. and a total dose of 2 M rad, post-irradiation annealing at room temperature caused the free radicals to disappear within a few minutes; by increasing the total dose to 5 M rad, free radicals stayed longer, at room temperature. When the total dose reached 50 M rad followed by heating at 160°C , which is higher than T_g, and lower than T_m, the initial signal decayed largely in 20 minutes without change in the spectrum's shape. Ref. (H2) irradiated polytetrafluoroethylene and obtained stable chain side radicals with very small amounts of chain end radicals confirming earlier results by Ref. (S10). The latter are not stable under irradiation and transform into chain side radicals. By oxygen and radiation rupture, all is transformed into chain end radical which transforms again to chain side radical. This is an example of a simultaneous formation of two free radicals, and the use of the E.S.R. technique to determine the decay of one and formation of the other. The effect of temperature was also investigated.

Ohnishi and Nitta (O1) found that gamma irradiation of PMMA in vacuum, builds free radicals' concentration up to a limiting value. They have also found that their rate of decay follows a second order mechanism. Shida et al. (S10) reported a first order decay below T_g for the above mentioned system during the first 20 minutes. The order was found to change at temperatures higher than T_g.

Tamura et al. (T2), studied the decay of free radicals formed through irradiation of four different kinds of polyethylene with 2 Mev electrons to a dose of 10 M rad. Both alkyl and allyl free radicals were detected. The alkyl radicals decayed much faster than the allyl. The effect of introducing monomer into the system showed that it apparently speeds up the decay of allyl radicals only. The decay was found to follow first order kinetics.

Nara et al. (N1), studied the decay of free radicals produced in irradiated polypropylene in the two temperature regions near 170°K and 260°K. The decay was found to follow second order kinetics in both temperature regions. Ref. (A5) reported that PEO free radicals decay slowly below T_g, with a sudden rise in the decay rate as the temperature rises above T_g.

2.12.2. Free radicals in irradiated solid monomers:

Radicals were found to be successfully trapped in irradiated monomers at low temperatures. Post-irradiation annealing at higher temperatures leads to rapid polymerization rates.

Atherton et al. (A7) used U.V. radiation to initiate the catalysed polymerization of methyl methacrylate and glycol dimethacrylate to form a copolymer. More radicals were found to be trapped in the copolymer as the DMA content is increased, the reason is that trapping is favoured by increasing crosslinking. Free radicals decayed 35% at room temperature while they lost only 7% at 0°C in a half hour.

Bowden and O'Donnell (B.18), subjected octadecyl methacrylate (m.pt = 12°C) to gamma radiation at (-196°C). This was followed by post irradiation annealing at (-30°C to 12°C). The conversion vs. time curves showed the typical post irradiation polymerization shape consisting of rapid initial rate followed by a sudden levelling off. The initial rate and limiting conversion were found to rise with radiation dose and temperature. When oxygen was allowed in, the rate decreased as a result of the oxygen being an inhibitor of free radical polymerization.

According to Ref. (K.2), radiation of malcimide monomer at 61°C in the solid state produced free radicals, which slowly decreased at 61°C . No post irradiation polymerization was observed, but free radicals decay followed first order kinetics. Irradiation was conducted at (-196°C), the concentration of free radicals was calculated and found to be 1.8×10^{17} f.r./gm., which decreases to 8.5% of the initial value if kept at 60°C for 24 hours. At 70°C, practically no free radicals were left after 24 hours.

Kaetsu et al. (K.1), irradiated glass forming systems (acrylamide and acrylic acid) and found that:

a) radiation at a temperature less than T_g causes no in-source polymerization but only rapid post irradiation polymerization on heating at a temperature higher than T_g due to the release of the peroxy radicals.

b) radiation at a temperature more than T_g causes in source polymerization and no post irradiation polymerization.

Decay of the E.S.R. signal in U.V. irradiated PMMA was studied by Ref. (M.7) attempting to solve the controversy between several investigators concerning whether the spectrum arises from a single free radical or two free radicals. While heating for 30 minutes at 110°C completely destroyed the E.S.R. signal, a rather broad single resonance remained after heating continuously at 80°C.

2.12.3. Concentration of trapped radicals and G-values:

Schneider (S. 2) irradiated commercial polystyrene with X-rays in vacuum at room temperature. He obtained a concentration of 3×10^{15} spins/ml for a dose of 10^{7} roentgens. Schneider encountered some difficulty due to a fast decay at room temperature. The E.S.R. pattern obtained was a triplet.

Ingram et al. (I2), detected no occluded polystyrene free radicals in the precipitated polymer, but reported a concentration of 10^{19} spins/ml as radicals trapped in low temperature glass. The shape of this signal was different from the usual three lines spectrum for polystyrene, in being a one broad line evidence of poorly resolved hyperfine interaction.

Florin et al. (F.1), obtained E.S.R. spectra for ordinary as well as for deuterated polystyrenes which were gamma irradiated. The Reported G-values are:

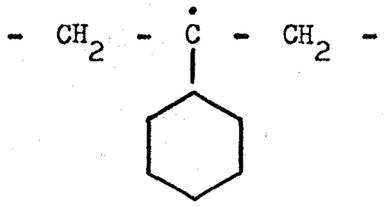
a) 0.08 for samples irradiated at 77°K and observed at 77°K and 300°K

b) 0.015 for samples irradiated at 300°K and observed at 300°K

Abraham and Whiffen (A3) irradiated polystyrene with γ rays at room temperature and obtained a triplet with a G-value = 0.2. Shields et al. (S1), obtained a single sharp line for x-irradiated polystyrene.

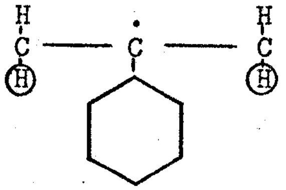
2.12.4. Free Radicals Structure:

Abraham and Whiffen (A3) discussed the spectrum's shape they obtained for polystyrene free radicals and indicated that at first it must be supposed that the main splitting arises from two equally coupled protons though the large line width obtained indicates that others may somewhat couple. Accordingly, the radical end $-CH\ (C_6\ H_s) - CH^{\cdot}_2$ is an obvious suggestion. However, this structure is very unstable and can achieve stability by delocalizing the unpaired electron over the aromatic ring and the radical structure, shown below, would probably be the right one:

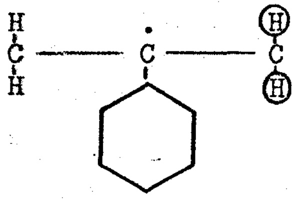


This is in accordance with Charlesby's (C 10) observation of the small yield of c-c fission. With appropriate geometry of the main chain one proton of each - CH_2 - would couple stronger than the other.

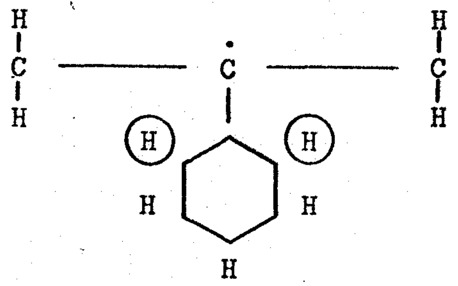
Florin et al. (F.1), through the study of γ-irradiated deuterium substituted polystyrenes revealed more about the hyperfine interaction. They suggested that the observed similarity of all deuterated polystyrene radicals spectra indicates that the possibility of having a strong hyperfine interaction with any main chain hydrogen is remote:



or



However, strong evidence is in favour of this radical. Accordingly, they concluded that the principle hyperfine interaction is with the two ring hydrogens in the ortho positions:



They excluded the possibility of positions other than the ortho by the fact that poly (p-deuterostyrene) and poly (m-methylstyrene) showed the same spectrum obtained for polystyrene free radicals.

CHAPTER III

METHOD OF APPROACH TO SOLVE THE PROBLEM

3.1. Available Information:

As outlined in (Chapter II), kinetics and mechanism of high conversion polymerization is complex. The kinetic scheme and assumptions that apply to the low conversion region were found to be not applicable to the high regions (D1, C4). The complexity is even greater at conversions higher than 90%, when the curves of conversion vs. time start to level off. Investigators have developed mainly qualitative, and partially quantitative theories about the middle conversion regions. It was found that the rate constants of termination, propagation, and possibly chain transfer are a function of the % conversion. This has been outlined in more detail in (Chapter II) and will be discussed more profoundly as applied to this investigation in (Chapter IV).

In order to appreciate the new approach taken to solve the problem (as outlined in Chapter I), a resume of relevant areas covered in the literature follows: The references given serve merely as examples; Chapter II however, is more elaborate in covering and discussing them.

i Thermal polymerization in bulk (no catalyst (B17,H10,H1 , R)).

ii Bulk polymerization using radiation energy (different types) at varried temperatures (C2, C3 , C 4, C11, D1, H3).

iii Irradiating monomers at very low temperatures, creating entrapped free radicals (practically no polymerization takes place during this stage), followed by post irradiation annealing at higher temperatures causing polymerization to occur at high initial rates

(B18, C1 , K1 , K2).

iv Irradiation of 100% polymer, at temperatures (well below T_{gp}) whereby sufficient trapping of the formed free radicals may occur, followed by post-irradiation at higher temperatures (occasionally over T_{gp}), enabling the investigator to study the free radicals' decay behaviour (A7, F1 , H2, K2 , N1, N2, O1).

One area seemed to be neglected i.e. creating trapped free radicals in a highly converted system by radiation, followed by studying their behaviour when annealed at higher temperatures.

3.2. Theoretical Approach:

This investigation was chiefly concerned with the behaviour of the trapped free radicals with respect to temperature. In order to accomplish this objective successfully, irradiated samples which are to be annealed must possess similar properties i.e.

a) Same % conversion.

b) Same molecular weight and molecular weight distribution.

c) Same free radicals concentration.

Once these are secured, experimental measurements can yield quantitative and qualitative data which might help to clarify the following:

i Free radical concentrations and G-values.

ii Order of termination mechanism.

iii Rate constants of termination mechanism.

iv Activation energies of termination.

v Effect of the glass transition temperature on ii, iii, iv.

vi Conversion vs. time curves as opposed to those with no pre-irradiation treatment (H10 H1) (see Fig. A & B).

vii Variation in the number average molecular weight during annealing.

viii The chemical structure of the trapped free radicals.

3.3. Experimental Approach:

Ref. (H3) provides conversion vs. time curves for styrene polymerization in bulk using gamma radiation. They cover three different dose rates, three different temperatures, and the whole conversion range (see Figs. C & D). With the help of that data, the following approach was adopted:

3.3.1. Experiments starting with styrene monomer:

By observing the same experimental conditions as those of other workers (H3), it would seem to be possible to develop monomer-polymer systems of prechosen conversions (e.g. 80, 90%), and follow the decay of free radicals by annealing at given temperatures, after irradiation. In this case, comparison can be made with Refs. (H1, H10) (see Fig. A & B).

This comparison, in fact, is not very accurate, due to the anticipated difference in properties (molecular weights etc.) of the two polymers. However, it will be shown later that the effect of these differences was found to be small in our case.

The dose rates to be used in polymerization are to be the same as the ones used by Ref. (H.3). Assuming success in obtaining post-irradiation polymerization curves, comparisons were to be made between them and:

a) Thermal bulk polymerization (conversion vs. time) curves carried out at temperatures identical to the post-irradiation annealing ones (B17 H10 R3), (see Fig. A & B).

b) Conversion vs. time curves for gamma irradiation induced polymerization at temperatures identical to the annealing ones (H3).

c) Each other, to determine the effect of:

- i Irradiation temperature and dose on the efficiency of free radicals' trapping (related to the $G_{R\cdot}$ value) and their chemical structure.
- ii The annealing temperature on the free radicals decay mechanism and rate.
- iii Temperature on the post-irradiation polymerization rate.
- iv Irradiation dose rate on the post-irradiation polymerization rate (see Fig.5.1 & 5.5 - 5.9).
- v % conversion at which the radiation-induced reaction is stopped, on the efficiency of free radicals' trapping.

In addition, variations in the number average molecular weight (if any), with the progress of post-irradiation polymerization, could be measured. The glass transition temperature's role in affecting:

- Free radicals' trapping efficiency.
- Free radicals' decay rate and mechanism.
- Post-irradiation polymerization rates.

were also to be investigated.

However, this last factor (T_g), proved to have a major role. Consequently, in all the investigated topics, a major portion has focused on it.

Experiments starting with monomer encountered several difficulties, which were found to introduce a certain degree of inaccuracy when attempting to interpret the results:

i Although polymerization curves (H3) (see Fig.C & D) were obtained with the use of the same monomer, experimental setting, and procedure; it was found that stopping the radiation-induced reaction at a predetermined % conversion was practically impossible; this might be attributed to:

a) The hot air feeding the radiation reactor was not effectively distributed.

b) Slight differences in dose rates received by samples irradiated at 4" and 6" distances from the centre of the source. (Chapter IV explains this point in detail.)

c) The extremely fast reaction in the region 40-90% conversion introduced a difficulty in estimating the exact time necessary to stop the radiation induced reaction at a predetermined % conversion.

ii It is established that polymers produced by using different dose rates will have molecular weights inversily proportional to the dose rate (B.5, C4, H3), and is therefore expected to affect the post-irradiation polymerization rates.

All these factors introduced a bulky obstacle, which prevented the achievment of complete similarity in properties (see section 3.2. in this chapter) between samples from two sets, theoretically intended to be irradiated at the same conditions i.e. theoretically identical.

3.3.2. Experiments starting with highly converted systems:

Two Monsanto samples (code name (c-1) and (c-2)) were used as starting material (see App. I for Chemical Analysis of samples). A major advantage of these samples is their very close molecular weights. In addition, having two different % monomer enables the study of the effect of % monomer on the rate of free radicals' decay.

Irradiation was chosen to be at room temperature. This choice was based on the following:

i The glass transition temperatures of the system (T_{gs}) of both samples were theoretically estimated (using a mathematical model relating T_{gp} to Q_p) to be greater than room temperature (see Chapter VI and App. IX) i.e. both systems were believed to be glassy at room temperature. Consequently, trapping of free radicals in high concentrations seemed to be highly probable.

ii Practically no polymerization in-source would be taking place (C.4), for relatively short irradiation periods. Consequently, the problem of starting the annealing process with sets of samples which are different in their % conversion or their properties, would be eliminated.

iii Irradiation of polymers, at room temperature, was often found in the literature (see Chapter II) to be a convenient means for successfully trapping free radicals, in concentrations high enough to be easily detected by the sophisticated Electron Spin Resonance technique.

A study of the effect of temperature on:

a) The rate of free radicals' decay.

b) The rate of post-irradiation polymerization.

could therefore be carried out quantitatively, in a convenient manner. To overcome any other difficulty, it was decided to apply one dose rate for a constant period of time to yield a fixed total dose. From previous dosimetry determinations (D1), and from those carried out along with the experiments, the dose rate at any specific date could be estimated with reasonable accuracy. Accordingly, the necessary time increase was added, to account for the source's strength decay, and to provide all irradiated sets with a constant total dose. Keeping a constant total dose, the very slight continuous decrease in the dose rate with respect to time, could be safely assumed not to have a measurable effect on the trapping efficiency. It was proved later that this assumption is justified, as the concentration of free radicals immediately after radiation $\left[R^{\bullet}_{o}\right]$ was found to be constant throughout the investigation.

Using the E.S.R. technique, several investigators reported the presence of free radicals in irradiated polystyrene; however, the identification of the structure is still debatable. Different free radicals' concentrations in irradiated polystyrenes have been reported ($3 \times 10^{15} - 10^{19}$ spins/ml) (A.2, A3, Fl, S.1, S.2). Variations in results depended upon:

a) Irradiation temperature.

b) Electron Spin Resonance measurement temperature.

c) Physical properties of the irradiated polymer.

d) Presence of air: during irradiation, during annealing, or during E.S.R. measurement.

e) Dose rate and total dose.

CHAPTER IV

EXPERIMENTAL WORK

Techniques and Theories

(1) Irradiation setting and geometry.

(2) Reaction vials.

(3) Sample preparation.

(4) Dosimetry.

(5) % conversion determination:

  i Gravimetric methods of analysis.

  ii U.V. spectrophotometric measurements.

(6) Measurement of free radicals' concentration using Electron Spin Resonance spectrometry.

(7) Determination of the number average molecular weight by Osmometry.

A brief theoretical background accompanies every measurement technique description, together with a sample calculation.

4.1. Irradiation Setting:

4.1.1. γ-rays Source:

A radiation laboratory (hot-cell) associated with McMaster Nuclear Reactor contains a cobalt-60 source used as a γ-ray emitter. The nominal source strength is 5,000 Curie, and is distributed in a cylinder 7" long, 3" I.D. The active material is distributed in the form of 12 rods 3/8" I.D. and 1 1/8" long. The hot-cell is provided with an observation window (made of lead glass), remote control manipulators, electric hoist, a water well for the source's storage, and a pass through system comminicating with the reactor pool. The reader is referred to Ref. (H.4) for an elaborate and more detailed description of the source and the hot-cell.

4.1.2. Irradiation reactor:

An aluminum box, 28" long x 18" wide x 28.5" high, placed on a table 27" high, was used as an air bath. Three sides were insulated with Ter-Test, the fourth, facing the hot cell's observation window, was made of methylmethacrylate sheet. A movable aluminum cover was used to allow the Co-60 source, in and out. An air blower was connected to one side of the box through a 4" diameter pipe at which opening in the box, a perforated plate evenly distributed the hot air. The air was heated in the duct by a 3,000 watt heater, and the temperature regulated by a De Khotinsky thermoregulator

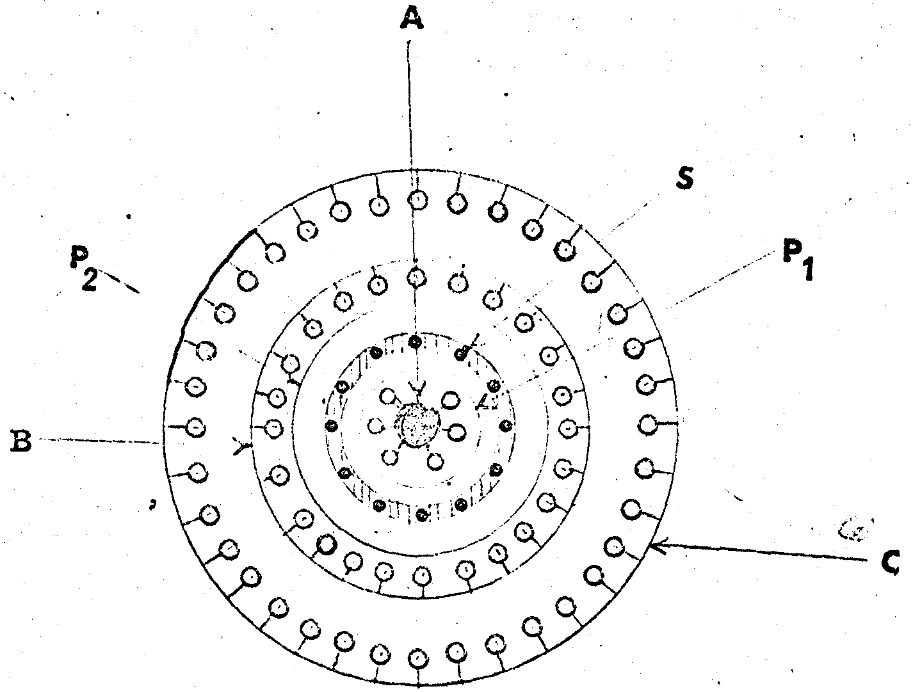
This arrangement's purpose, was to provide a constant temperature air bath within about ± 0.2°C. It was found later, however (H.3), that a temperature gradient existed, caused by a poor distribution of the hot air influx.

4.1.3. Reactor's Geometry and its effect:

Figure (4.1) is a diagram showing the reactor. In the centre, 6 sample holders are mounted on a metallic rod A , S is the radiation source distributed in the form of 12 rods of cobalt-60. B is a metallic concentric cylinder carrying 24 sample holders which are at 4" distance from the centre. C is a larger metallic concentric cylinder carrying 36 sample holders which are at 6" distance from the centre. P_1 and P_2 are 2 metallic concentric cylinders which are used to protect the vials mounted on A and B from being broken in case the source struck any of them while being placed. Self screening is thought to be partially responsible for the observed irreproducibility of conversion vs. time plot

REACTORS GEOMETRY

FIGURE 4.1



during irradiation (C13). Considering two runs, although there will always be a constant distance between the C, B and A cylinders and the source, no guarantee can be made that a constant distance exists between each individual Co-60 rod on one hand, and a sample position on any of the cylinders on the other hand. In addition, for the B and C samples, it is obvious that for the former, every second position receives equal amounts of dose, and for the latter, equality is for every third position only. This results in putting an upper limit on the number of identical positions (12) i.e. equal to the number of co-60 rods.

In the second part of the investigation, the temperature gradient problem did not exist, since irradiation was carried out at room temperature, and the irradiation geometry problem was solved by marking the C cylinder at two locations opposite to each other, in line with a third mark on the observation window. In placing the source in position, care was taken in order to bring the two arms of the source's handles to fall on the same line as the three artificially made marks. This insured a constant position for the source.

4.2. Sample reactor vials:

Annealed Pyrex vials, of approximately 10 c.c. in capacity, were used to contain the irradiated samples (whether monomer, or polymer-monomer system). The vials had a constricting neck ending in a standard male tapered joint B 14. The loaded vials, were connected to the degassing system, and evacuated, with the monomer frozen in liquid nitrogen. After sealing, the samples were brought to room temperature, and irradiated under appropriate conditions.

4.3. Sample preparation:

Two types of samples were used. This caused only a slight difference in the procedure.

4.3.1. Vials Filling:

i Starting with styrene monomer (uninhibited, kept in dark bottles, at refrigerator temperature), a 10 c.c. hypodermic syringe was used to introduce the monomer into the vials; this was due to the narrowness of the vial necks which prevented the liquid from flowing freely. The syringe was fitted with a 6" stainless steel needle which helped to introduce the monomer into the wide bottom part of the vial without touching the walls of the narrow upper parts.

ii When starting with solid (c-1 or c-2), samples (see App. I for chemical analysis) slow direct introduction was possible.

4.3.2. Degassing:

Oxygen acts as a free radical scavenger. Therefore, before samples' irradiation, they must be thoroughly degassed. Numerous investigators have reported the effect of oxygen on: polymerization rate (B18), free radicals decay (C.1, K.2), and on the shape of the obtained spectrum (K.2, H2), as has been shown in detail in (Chapter II). A brief description of the degassing procedure follows:

- Greasing the vials' mouths with silicone high vacuum grease.
- Connecting the empty vials to the vacuum system (see Fig4.2) which can handle 8 samples at a time, and are tested for any leaks, using a leak detector coil.
- The valves connecting the vials to the system are closed, vials disconnected, and filled with samples as previously described.

- Greasing is repeated if necessary.
- The filled vials are connected to the system (valves still closed), and Dewar flasks filled with liquid nitrogen are mounted to be used as freezing baths.
- 15 minutes freezing while system is under about 10^{-3} H_g vacuum.
- Valves are then opened and degassing is allowed for 15 minutes.
- For styrene monomer:

  Close valves, replace liquid nitrogen baths with warm water ones causing thawing. This will expel any air traces entrapped. Refreezing (15 minutes), and degassing (15 minutes), still using the primary pump only.
- For both samples again:

  Valve A is then shifted to be connected only to the mercury diffusion pump, and valve B is opened. The system is then under 10^{-6} mercury and this is allowed to continue for at least 15 minutes, preferably a half hour.
- Close valves, remove liquid nitrogen baths.
- Sealing of the vial necks follows, using oxygen flame.
- The degassed samples are placed at refrigerator temperature until used for irradiation.

Remark:

Vials should be chemically clean. This can be achieved by:

- Filling them with boiling 1:1 H_2SO_4:HNO_3 acids, and leaving them for a few hours..
- 5 times washing with tap water, 5 times with distilled water and 3 times with acetone.

- 1-2 hours drying in an oven at about 120°C.

4.4. Dosimetry:

4.4.1. Introduction:

The unit for the absorbed dose, the rad, is increasingly being used in radiation chemistry. It is clear that the absorbed dose depends on the properties of the particular medium in which it is measured. The absorbed dose is defined by the amount of energy per unit mass received by a material exposed to ionizing radiation at the place of interest (W.5).

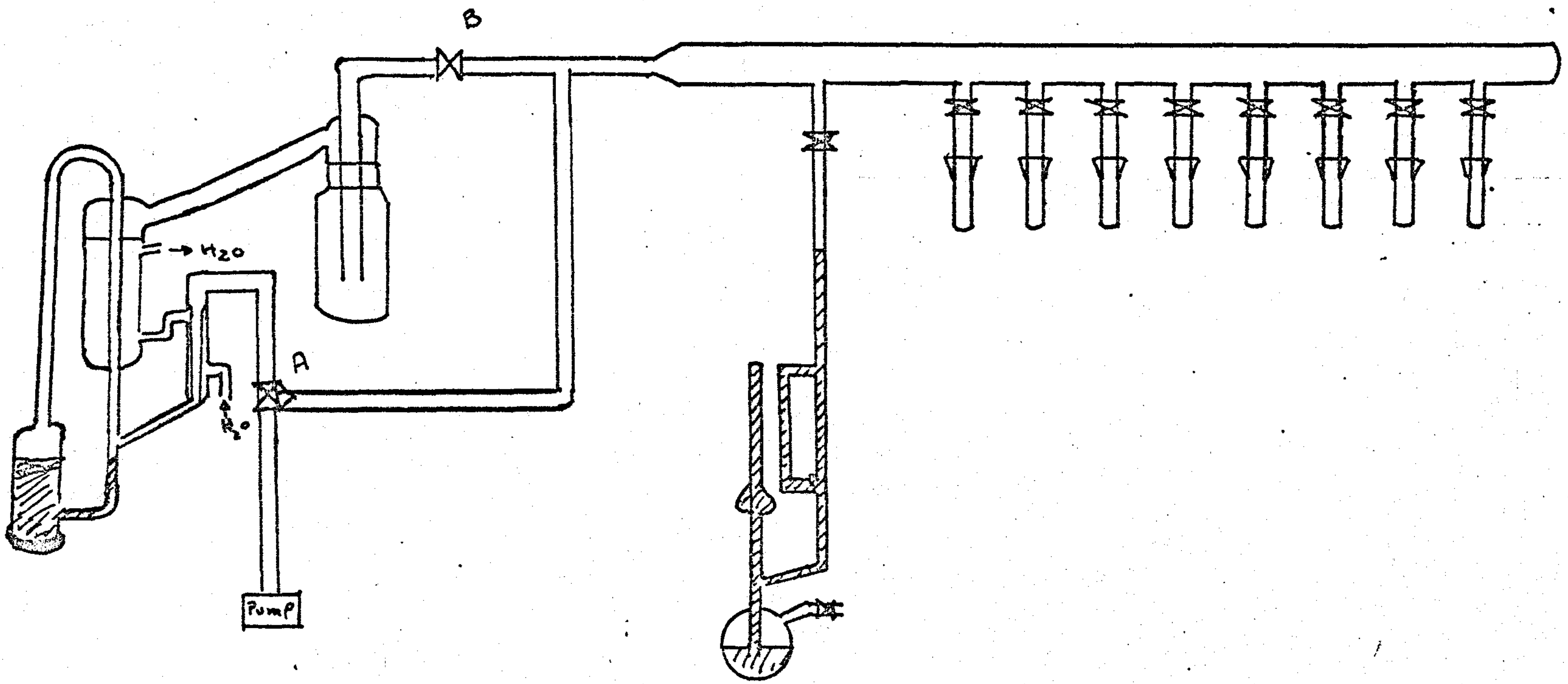
Experimental methods designed to determine the absorbed dose have been long known. The majority of the early ones relied on measuring the ionization produced in air caused by radiation. However, the difficulty lay in relating this value to the energy absorbed by the irradiated matter. Calorimetric techniques are used to determine the absorbed dose directly in fundamental units. Microcalorimetric ones are much more accurate. The disadvantage of these methods is that in the former case, the accuracy is poor due to the extremely small amount of energy usually dissipated from sources, while the latter method is considered tedious and time consuming. These methods can be used to determine the strength of the source. Once this is known, indirect methods using secondary indicators, can be used for routine measurements, as long as they can show a constant response over as wide as possible a range of intensity.

4.4.2. Fricke Dosimetry:

This is a successful method that has long been used for diosimetry using a secondary indicator which possesses the above mentioned property, and in addition, is simple and relatively fast. Swallow (S18), presents this technique in detail. Briefly, it is based on the oxidation of the

VACUUM SYSTEM

FIGURE 4.2



ferrous ion in a ferrous sulfate solution to the ferric ion, by radiation, using spectrophotometric measurements for the determination of ferric ions, which can be determined with high accuracy at the absorption peak of 3040 Å. The G value for this oxidation reaction when Co-60 -radiation is used, amounts to 15.5 (S18). The yield of ferric ions is proportional to the absorbed dose for doses between about $10^3 - 10^5$ rads (W.5). The low sensitivity of this system, restricts it to the measurement of large doses. However, very accurate results are usually obtained if the total dose lies between: $1 \times 10^{18} - 2.4 \times 10^{18}$ e.v/gm (S5). The absorbed dose in this system is calculated using the relation:

$$D_t = 2.94 \times 10^4 \left(1-0.007\,(t-20)\right) \text{O.D.} \qquad 4.4.1.$$

D_t = total absorbed dose in rads

t = the temperature in °C at which O.D. is measured.

O.D. = optical density of the irradiated solution.

$$\text{dose rate (rads/sec)} = \frac{\text{absorbed dose in rads}}{\text{time of irradiation (seconds)}} \qquad 4.4.2.$$

The absorbed dose in the polymer system can be then derived from the experimentally measured one for the Fricke solution. The following formula is used for this purpose:

$$D_p = D_f \left(\frac{u}{\rho}\right)_p \left(\frac{\rho}{u}\right)_f \qquad 4.4.3.$$

where:

D_p = Dose rate for the polymer system.

D_f = Dose rate for the Fricke solution.

$\frac{u}{\rho}$ = The mass energy absorption coefficient of each system as indicated by the subscripts, and is a measure of the stopping power of the system.

4.4.2a. Experimental Procedure:

1) Fricke solution preparation:

i Triply distilled water was used, and was obtained by repeated distillation of an alkaline permanganate solution, made by adding a few NaOH pellets to 0.1 N potassium permanganate solution ($KMnO_4$)

ii This water was used to make about 10^{-3}M ferrous ammonium sulphate (AR reagent) $\left[(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O \equiv 392.16\right]$, in 0.1 N reagent grade sulfuric acid, which contains approximately 10^{-3}M Na Cl.

iii Oxygen was bubbled in the obtained solution for a few hours, after being passed in concentrated sulfuric acid to remove any organics from the gas.

iv The oxygen saturated solution is then kept in a dark brown glass bottle until used.

v Fresh solutions had to be prepared each time new dosimetry is attempted if the time lapse between the two is more than a few days. If only one or two days have lapsed since its preparation, resaturation with oxygen is the only additional step.

2) Dosimetry Vials:

Vials similar to those used for polymerization, (except for not having a ground joint at their mouths) were used for dosimetry. These vials must be extemely clean before being filled with 10 ml of Fricke solution. This was done by using boiling concentrated H_2SO_4:HNO_3 1:1 followed by 10 times thorough washing with distilled water, using triply distilled water during the last three or four times. The last washing step uses the Fricke solution itself.

3) Vials Positioning:

The vials when irradiated, were connected to the sample holders and at the same positions used for the polymerization reactions.

Previous Dosimetry data were available (D.1). Consequently, the approximate time needed for irradiating the Fricke solution at each position to give accurate results, could be estimated. Table (4.3.) shows the late Dosimetry measurements at different positions.

After irradiation, the amount of absorbency of each sample was obtained by using a Beckman D.K. spectrophotometer set at 304 mu. Base line checking was repeated after each sample using non-irradiated Fricke solution in both cells. The accuracy was also checked by measuring the transmittance occasionally and checking that the

$$\text{absorption} = \log_{10} \frac{1}{\text{transmittance}}$$

In determining the dose rates at positions B and C , every second position and every third position satisfies the equality need, as was mentioned before. However, no difference could be detected when adjacent positions were measured experimentally.

4.4.2b. Results and Calculations:

The following is a sample calculation:

TABLE 4.1.

4"	Sample code number	Position	Time of irradiation in seconds	Absorption	Average
4"	112	4	420	81.5	82
4"	113	8	420	83	
4"	114	5	420	82	
4"	115	9	420	81.5	

Substituting with the average value of absorption in equation 4.4.1. to calculate the total dose D, using the latter in equation 4.4.2. Therefore, the dose rate = 53.38 rads/sec.

TABLE 4.2.

4"	Sample code number	Position	Time of irradiation in seconds	Absorption	Average
4"	116	4	240	48	46.5
4"	117	8	240	45.5	
4"	118	5	240	45.5	
4"	119	9	240	47	

Similarly from the given table a dose rate of 52.96 rads/sec is obtained. Therefore, the average dose on this date at 4" = 53.17 rads/sec.

A summary of the experimentally obtained dose rates by Fricke Dosimetry is shown in Table 4.3.

Table 4.3.

Date	Dose rate in rads/sec.		
	1"	4"	6"
10-4-69	176.7	58.3	
10-7-69	166.5	53.2	21
8-9-69	170.3		
12 11-69	167.0		
15-12-69	165.2		

The constraint of short irradiation time in the case of 1" measurements causes this highly precise technique to be vulnerable to errors up to five percent (S.18).

The experimentally determined dose rates are those absorbed in water. In order to determine their counterpart in the polymer, equation (4.3.) was used. However, the values of the mass energy absorption coefficients for polymer and water must be known.

Given any compound $X_a Y_b$, its mass energy absorption coefficient for a given photon energy can be calculated from the relation:

$$\left(\frac{u}{\rho}\right)_{X_a Y_b} = a W_x \left(\frac{u}{\rho}\right)_x + b W_y \left(\frac{u}{\rho}\right)_y \qquad 4.4.$$

where:

$\left(\frac{u}{\rho}\right)_x$ & $\left(\frac{u}{\rho}\right)_y$ = the mass energy absorption coefficients of the elements x and y.

W_x and W_y = the ratio between the weight of elements, x and y and the compound's total molecular weight.

a and b = the unit's number of each element in the compound

Accordingly, $\left(\frac{u}{\rho}\right)$ for styrene and polystyrene are practically the same. Ref. (W.4) lists the value of $\frac{u}{\rho}$ for several compounds and elements. It was found that:

$$\left(\frac{u}{\rho}\right)_{styrene} = 0.02876$$

$$\left(\frac{u}{\rho}\right)_{water} = 0.02970$$

According to equation (4.3.), using an absorbed dose rate in water of 168 rads/sec. as an example, therefore:

$$D_{polymer} = \frac{168 \times 0.02876}{0.02970} = 162.7 \text{ rads/sec.}$$

As the dose rate is constantly decreasing with time, a slight calculated increase in the radiation time is added when the aim was to use a constant total dose throughout the investigation, (as in the case of irradiation of (c-1) and (c-2), at room temperature).

4.5. Percentage Conversion determination:

When polymerization is in progress, the proportion of polymer to monomer steadily increases. In order to measure this change experimentally, several methods are available, the best known is based on separating the polymer and monomer.

4.5.1. Gravimetric method of analysis:

Two types of samples were handled.

- Starting with monomer, polymerizing it at 85°C or 50°C by radiation.
- Starting with (c-1) and (c-2) (see App. I for chemical analysis) irradiation at R.T. to create free radicals (practically no polymerization takes place during this step).

After irradiation, one vial is immediately quenched in liquid nitrgen and processed for conversion determination at time zero. The rest of the samples are annealed at the desired temperature. Post-irradiation annealing was carried out in a hot air oven, whose temperature control is about ± 1°C (except for the cases where the investigation was at room temperature. Temperature varied within ± 1.5°C).

In the case of (c-1) and (c-2) samples, the rate of post-irradiation change is high at elevated temperatures, causing the time intervals between each two samples to be short. In order to overcome the error caused by the time factor needed for a sample to acquire the oven temperature, a metallic socket, heated by an electric coil and connected to an autotransformer, was used to heat the samples up to the desired annealing oven temperature in about one and a half minutes. The necessary variac setting for each temperature was determined by trial and error, using a thermocouple and a stop-watch.

At the end of the required post-irradiation annealing time for a sample, the vial is quenched in liquid nitrogen to stop any further reaction, and samples for % conversion or E.S.R. measurements are taken by breaking the vial. The rest of the procedure is as follows:

- About 1-2 gms of sample are weighed accurately.
- Approximately 50 ml of dioxane are used to dissolve the polymer with about 0.1 gm of hydroquinone inhibitor added to prevent any further polymerization.
- Complete dissolution is accomplished by allowing samples to sit for two days.
- Precipitation of the polymer is achieved by adding the dioxane solution drop by drop to 15 fold excess of methanol, stirred with a magnet.
- The precipitate is allowed to settle for a day, then is filtered through fine pores sintered glass 50 ml crucibles, using a vacuum filtration set that holds four samples simultaneously.
- The precipitate obtained contains all the polymer with the exception of such small molecules as dimers or trimers which might pass to the filtrate with the monomer.
- A vacuum oven set at 65-70°C is used for drying the precipitate. The oven is connected to a suction pump through a vapour trap where dry ice is used as a cooling medium together with some methyl alcohol.
- Weighing the polymer will yield the % polymer in the original polymer-monomer sample.

The gravimetric method is fairly accurate but its absolute error would be considered relatively high for investigating conversion at the last 5% monomer. A good method for estimating traces of monomer is the use of the U.V. spectrophotometry. Its absolute accuracy is the best for the last 2% monomer, but the more the % monomer, the lower the accuracy.

4.5.2. % Conversion determination by U.V. spectrophotometry:

U.V. spectrophotometry is a relatively rapid and accurate method for the determination of monomeric styrene in a polymer-monomer system. It is most suited and highly efficient in determining concentrations with the last 2% unpolymerized monomer. It can be used for higher monomer concentrations by diluting the investigated solution, but this would naturally lower the absolute accuracy. When % monomer is around 10%, it is advisable to determine it both gravimetrically and spectrophotometrically as a double check.

Styrene absorbs U.V. radiation 40-100 times as strongly as polystyrene at 245 mu wave length. The experimental procedure steps extracted from **Ref. (I.3) follows:**

1) Approximately 0.1 gm of polymer sample is weighed into a 100 ml Erlenmeyer flask. 50 c.c. of reagent grade chloroform is added by means of a burette.
2) The solution is allowed to sit overnight to ensure the dissolution of the polymer present.
3) 10 ml of the above solution are added with agitation to 90 ml (delivered accurately by a burette) methanol in a 125 ml Erlenmeyer flask to precipitate the polymer.
4) The resulting solution is filtered through a sintered glass crucible (no vacuum applied) and the filtrate is used for absorption measure-

ment.

5) The reference standard is 10% chloroform in methanol (accurately measured by means of a burette).

Note: Care must be taken that the reference solution is prepared in a similar manner to that of the solution containing the polymer (exactly the same chloroform: methanol ratio). Otherwise, chloroform and methanol are present in different relative quantities, and the result will be affected.

Remark:

It is necessary to check for base line drift occasionally by filling the two cells with the reference standard and checking for the 0% and 100% absorption. A calibration curve for the abosorbance vs. styrene concentration (Fig. 4.3.), (Ref. H.3) was used in determining the % styrene monomer. The reader is referred to the D. K. Beckman U.V. spectrophotometer manual for operational detail.

Sample Calculation:

Assuming an absorption = 0.2 therefore mg styrene/100 ml = 1.14 from calibration curve) this value is equivalent to the amount of styrene in the solution (10 chloroform + 90 methanol).

Therefore, dilution factor = $\frac{50}{10}$ = 5

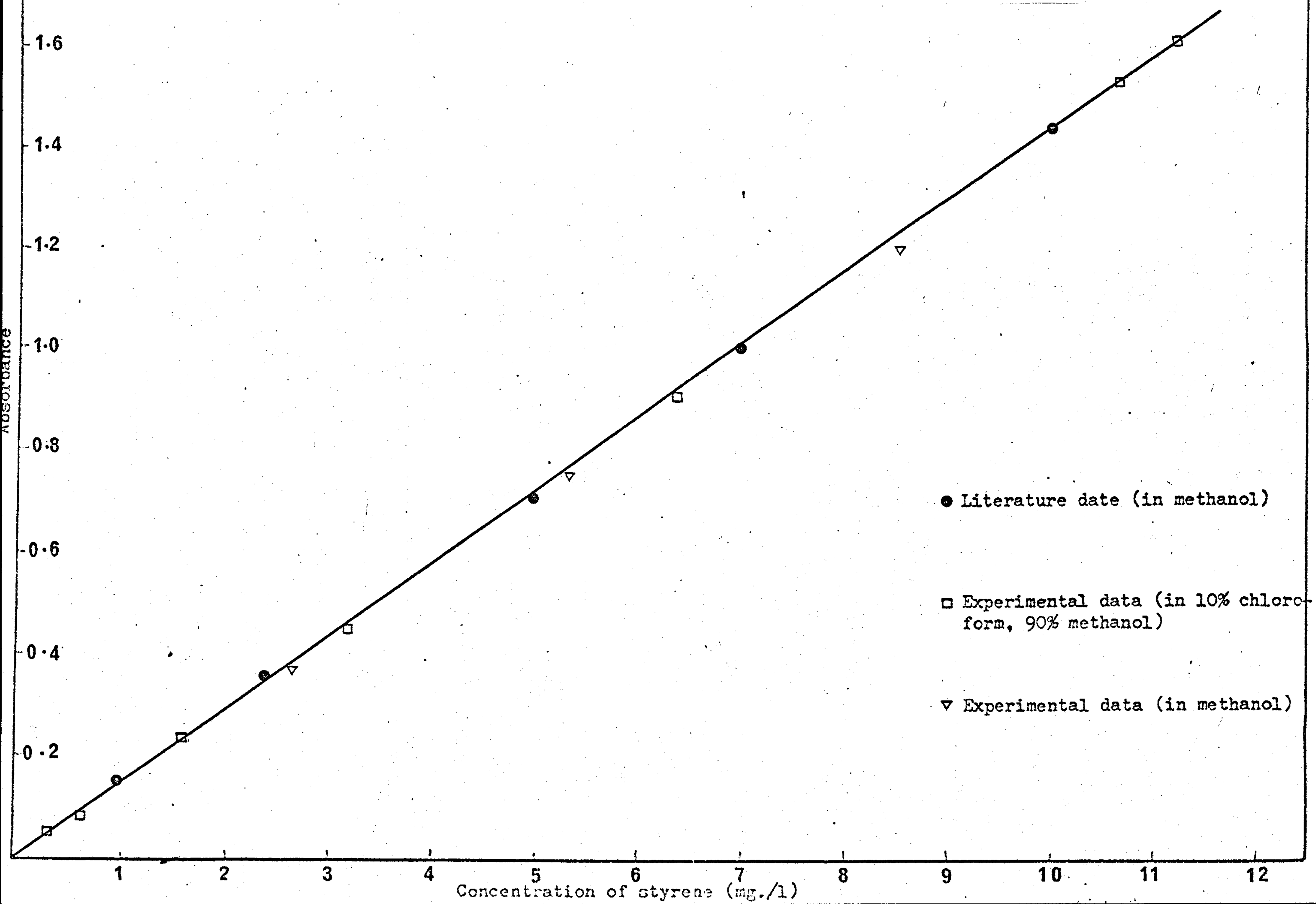
Therefore mg styrene in the sample = 5 x 0.14 = 0.70

Assuming sample weight = 0.1 gm

Therefore % styrene $= \frac{0.7}{1000(\text{gms})} \times \frac{1}{0.1}(\text{wt}) \times 100(\%) = 0.7\%$

Therefore % conversion = 100 - 0.7 = 99.3%

Note: Styrene monomer is miscible in all proportions with methanol (B.17). Polystyrene is insoluble in methanol (B17) (tested by Staudinger and



Calibration Curve: Spectrophotometric Analysis of Styrene. (H3) FIGURE 4.3

Heuer for two molecular weights 130,000 and 5,000 and found insoluble in both cases). On the other hand, it is completely soluble in both chloroform and dioxane.

4.6. Electron Spin Resonance Spectrometry:

4.6.1. Introduction:

Chapter II showed how free radicals play the major role in the process of polymerization. Their characteristics have been covered in detail. In order to acquire some information concerning their behaviour, they must be generated in large concentrations, at conditions such that their recombination is relatively slow to provide the investigator with sufficient time to detect and study them.

Numerous techniques of free radicals' detection are known. The E.S.R. technique is the most selective and most sensitive for singling out free radicals. The technique also has the advantage of being able to determine concentrations. In some cases, identification of free radicals could also be achieved. The two major disadvantages of the E.S.R. spectrometry technique are:

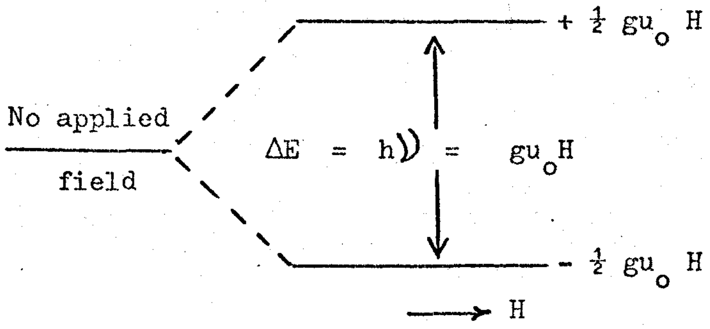
1) The centering of all E.S.R. spectra around the same value of g which causes a troublesome superposition of spectra.
2) The recorded spectra are given in terms of the derivative of absorption with respect to the magnetic field.

4.6.2. Simplified Theory of E.S.R:

The E.S.R. technique is based on using the main property of free radicals i.e. having an unpaired electron and a magnetic moment associated with it. A detailed discussion of the theory can be found in the literature (A.4, I.1). However, some basic theory is briefly given to help appreciate the scope and limitations of E.S.R.

The odd electron orbiting around the nucleus possesses an angular momentum in addition to a spin angular momentum caused by its spinning. This spinning can give rise to a rotating magnetic dipole which acts like a small magnet.

Under the effect of an external D.C. Magnetic Field, the magnet will orient itself in a definite direction. Electrons possessing moments in the applied filed's direction will align themselves in the same direction. On the other hand, those spinning in the opposite direction, will be aligned anti parallel to the applied field's direction. The latter is an unstable state and has a higher energy position, and is accompanied by an energy absorption. The diagram shows the separation of electrons into the two energy levels. The principle of E.S.R. is simply to make accurate electron translations of the observed transition from the low energy level to the higher one, with the absorption of energy $\Delta E = h\nu$ (I1, W3):



h = planks constant
ν = frequency

$$h\nu = gu_o H$$

The obtained splitting which was caused by a magnet, if subjected to a radiation of frequency ν, so that the quantum $h\nu$ is equal to the energy difference between the two levels, will cause resonance to occur between them.

The impinging energy is absorbed by electrons in the lower energy level causing them to excite to the upper level. Simultaneously, the upper level electrons emit radiation of frequency ν and fall to a less excited level. For any system in thermal equilibrium, more electrons lie in the lower level than in the upper one, hence, a net absorption of radiation of frequency ν.

The Maxwell-Boltzmann expression gives the numerical ratio of the electrons in the two states:

$$N_1/N_2 = \exp(-\Delta E/K_B T) \qquad 4.5.1.$$

N_1 = number of electrons in the upper state

N_2 = number of electrons in the lower state

ΔE = the separation between the two levels

= $h\nu$

K_B = Boltzmann constant

T = the absolute temperature

and the whole relation is very close to unity (I3).

Consequently, greater sensitivity is usually obtained by measuring at lower temperatures, to increase the difference between N_1 and N_2. The resonance is able to continue due to some other mechanism apart from the stimulated emission. More details can be found in Ref. (I1).

The following relation gives the energy difference between the upper and lower states in terms of the magnetic field:

$$\Delta E = g u_o H \qquad 4.5.2.$$

g = called the "g-factor", and is a physical property of the electron and is a dimensionless constant.

u_o = Bohr megneton.

H = The magnetic field intensity in the apparatus' direction.

To summarize, an equation in the form:

$$\Delta E = h\nu = gu_oH \qquad 4.5.3.$$

is the basic relation of the E.S.R. spectrometry, and only an electromagnetic quantum of this frequency will cause a transition between the two states to occur. The equation represents resonance between the quantum energy and the energy difference between the two levels.

The E.S.R. spectrometer is designed in such a way so as to detect the microwave energy absorbed by the free radicals present, from which the number of free radicals can be obtained. The spectrum shape obtained was very similar to those found in the literature for irradiated polystyrenes.

4.6.3. Experimental Technique:

In the present investigation, irradiation and post-irradiation annealing were both carried out under vacuum. However, the vacuum was broken immediately after annealing and samples were stored at liquid nitrogen temperature in N.M.R. tubes placed in a dewar flask, to preserve the free radicals. During the few minutes needed for E.S.R. measurement, samples were taken out of the liquid nitrogen bath, allowed to warm up to room temperature, and placed in an E.S.R. tube. The signal's shape remained practically unchanged during the decay runs (emphasizing the presence of one type of free radicals).

The instrument used in the present investigation is a spectrometer type JES-3BS-X (Japan Electron Optics). Spectra are measured in the neighbourhood of 9200 mc/sec. The reader is referred to the manual for operational details.

The recorder in the E.S.R. spectrometer yields the first derivative of absorption. The number of spins is proportional to the area under the absorption curve. In order to determine the absolute free radicals' concentration, the area under the absorption curve of the sample should be compared with that under the absorption curve obtained for a sample of radical concentration. $\alpha\ \alpha'$ Diphenyl-β Pycryl-Hydrazyl (DPPH) was used as such a standard. Since polystyrene free radicals are extermely stable at liquid nitrogen temperature, it was used as a secondary standard for free radical concentration determination. Samples chosen for this purpose were those for which no post-irradiation annealing was performed, i.e. zero post-irradiation time $\left[R^{\bullet}_{o}\right]$, and were always kept under liquid nitrogen. As will be seen in Chapter V, the free radicals' concentration were:

a) For (c-1) samples = 1.9×10^{17}/gm
b) For (c-2) samples = 2×10^{17}/gm

Care was always taken for the spectrometer settings to be the same in all cases.

In order to yield areas under the absorption curves, it was necessary to perform a double integration of the first derivative recorded signals. Wyard (W.7), suggested a fairly fast and accurate method. The method is one of numerical integration. On the first derivative spectrum, the magnetic field is divided into n intervals, each of length h, the value Y of the ordinate is written down. Wyard derived a double integration formula which also corrects for basis line drift:

$$A = \tfrac{1}{2} h^2 \sum_{r=1}^{n} (2n - 2r + 1) Y_r \qquad 4.6.1.$$

The formula was used to obtain the numerical free radicals concentration in polystyrene secondary references by comparing their obtained areas to that obtained from the DPPH standard of known free radicals concentration using the same spectrometer settings:

$$N_1/N_2 = A_1/A_2 \qquad 4.6.2.$$

For signals whose shape does not change while decaying, as observed for polystyrene free radicals, peak heights were used for relative decay comparison, with only the first sample undergoing the double integration technique vs. the secondary standard, as a double check:

$$N_1/N_2 = H_1/H_2 \qquad 4.6.3.$$

DPPH possesses one unpaired electron in each molecule, i.e about 1.53 x 10^{21} spins/gm. This necessitates that a minute weight would be taken as a reasonable standard, which would probably be coupled with a weighing error. Mixing with a diluent as starch free of free radicals, overcame the weighing problem, but the homoginity of the mixture was doubtful. A DPPH solution in benzene of 1 m M/L, was finally used as a primary standard (B12, V2).

The G-value of polystyrene reported by Ref. (A.3) is = 0.2. The one obtained in this investigation is about 0.43 (see Chapter V). Both values are to be taken as very approximate (a ± 50% is the approximate expected accuracy.

On the other hand, relative decay studies are much more accurate and successful, especially in cases where the spectrum's shape does not change while decaying.

4.7. Determination of the Number Average Molecular Weight by Osmometry:

4.7.1. Theoretical background:

If a solution is separated from the pure solvent by a barrier permeable to solvent molecules only, a difference in chemical potential (u) will be taking place, being less for the solvent in the solution, than that of the pure solvent. To keep the system's equilibrium, i.e. to equalize the solvent's chemical potentials (u) on both sides of the barrier, an excess pressure may be applied to the solution. The required excess pressure is known as the osmotic pressure π, and is related to the change in chemical potential by:

$$\Delta u_1 = -\pi V_1 \qquad 4.7.1.$$

where V_1 is the molar volume of the solvent. For very dilute solutions:

$$\pi V_1 = -RT \ln x_1 = RTx_2 \qquad 4.7.2.$$

where x_1 and x_2 represent the mole fractions of solvent and solute. As the solute concentration tends to zero:

$$x_2 \cong \frac{C_2 \ V_1}{M2} \qquad 4.7.3.$$

where C_2 = solute concentration in g/cm^3 of solution

M_2 = solute molecular weight.

At infinite dilution:

$$\left(\frac{\pi}{C_2}\right)_o = \frac{RT}{M_2} \qquad 4.7.4.$$

From equation (4.7.4.) if it holds over a finite range of solute concentrations, plotting $\left(\frac{\pi}{C_2}\right)_o$ vs. C_2 will yield a straight line parallel to the C_2 axis. Consequently, any π measurement would yield the correct M_2 value. However, for polymeric solutions, deviations occur, and the resulting line is not parallel to the C_2 axis. According to Ref. (M.5), the relationship for a real solution's osmotic pressure could be expressed in the form of a virial equation:

$$\frac{\pi}{RTC} = \left(\frac{1}{M} + A_2 C + A_3 C^2 + \ldots\right) \qquad 4.7.5.$$

where A_2 and A_3 are the second and third virial coefficients. The terms in c equal to and above the second power are very small. The slope is practically equal to the second virial coefficient A_2 which represents the solvent - solute interaction.

4.7.2. Experimental Technique and Calculation:

A high speed membrane osmometer model (Hewlett-Packard model 502) was used for Mn determination.

Samples were dissolved and precipitated following the same experimental steps as in the % conversion determination outlined earlier in this chapter.

A known weight of the resulting polymer was then dissolved in toluene in a concentration of about 10 gm/l. Three dilutions were prepared very accurately, resulting in 4 different concentrations to be used for osmotic pressure measurements. The osmotic pressure for each solution is the difference between the final digital counter reading and that found for the solvent. The obtained value π, is divided by the concentrations in gm/litres, and the extrapolated value at zero concentration is the one used for molecular weight calculation:

$$\left(\frac{\pi}{C}\right)_{C \to 0} = \frac{RT}{Mn}$$

π = osmotic pressure

C = concentration

R = gas constant

T = absolute temperature in degrees Kelvin

Mn = number average molecular weight

The value of "R" in litre atmosphere degree^{-1} mole^{-1} equals 8.205×10^{-2}. This is converted to pressure units of cm of toluene by multiplying by cm of toluene per atmosphere, which will depend on the toluene's temperature. For most purposes the value of (0.862) which is the toluene's density at 25°C can be used, since it varies 1% per 9°C. The value of "R" then is:

$$8.205 \times 10^{-2} \times 1026/0.862 = 97.66$$

where 1026 cm is one atmosphere of water.

The temperature used was 30°C accurately controlled by the instrument. Therefore:

$$RT = 97.66 \times (30 + 273) = 2.96 \times 10^{4}$$

(App.10) represents a numerical example, and a typical plot showing the extrapolated line used to obtain $\left(\frac{\pi}{c}\right)_{c \to 0}$. Mn was therefore obtained by a straightforward calculation.

4.8. Determination of the Temperature inside the vials:

It will be shown later in Chapter V, that the post-irradiation reaction is fast, at $T > T_{gs}$. The reaction is exothermic, consequently, a possibility exists that some heat is being generated faster than it could be dissipated.

A copper-constantan, and a Chromel-Alumel thermocouples were chosen to measure the temperature inside the vials. About 1" long 1/8" I.D. side connection, was attached to the reaction vials at their narrowest part of the neck, and thermocouples were inserted and sealed. Results of measurements were as will be shown in Chapter V, with the maximum being for (c-1) samples at $170^\circ C \pm 1 \longrightarrow 172 \pm 1.5^\circ C$.

CHAPTER V

Sequence of Experimental Study

The prime aim of this investigation, was to identify the conditions (% conversion, temperature, and dose rate) necessary for trapping high concentrations of free radicals in highly converted styrene-polystyrene systems.

Post-irradiation annealing at varied temperatures, aimed at investigating the following areas:

a) Polymerization rates during post-irradiation annealing.

b) Trapped free radicals, their rates of decay and mechanism, during post-irradiation annealing.

c) Changes in M_n during post-irradiation annealing.

For a quantitative treatment of (a, b and c) to be possible, sets of samples must be identical before annealing (% conversion, molecular weights, and free radical concentration).

Two courses for the investigation have been followed:

i) Experiments starting with styrene monomer

This procedure did not prove to be suitable for quantitative deductions. However, some qualitative deductions were reached, which helped selecting a better course for the investigation, namely: part (ii).

ii) Experiments starting with highly converted samples (c-1 and c-2) (For analysis, see App. I).

This procedure, on the other hand, proved to be convenient for qualitative and quantitative analysis.

Definition:

The term "set of samples" is applied to both cases (i) and (ii), and represents a number of samples which normally undergo the following steps:

1) Degassing.
2) Irradiation at a certain temperature.
3) Post-irradiation annealing at a chosen temperature, and the sequential removal of samples from the oven, in order to determine the following properties, as a function of time:
    a) The concentration of free radicals (if present), using the E.S.R. technique.
    b) The % conversion, using gravimetric or U.V. spectrophotometric analysis.
    c) The number average molecular weight M_n, using the Osmometry technique (performed on three sets only).

5.1. Experiments starting with Styrene Monomer:

a) Using data curves from Ref. (H3) (Fig. C & D) radiation induced polymerization was performed on sets of samples at 50°C and 85°C. Irradiation was stopped when the system theoretically reached a predetermined % conversion (e.g. 90%). However, a great number of difficulties arose, which made it impossible to obtain the desired % conversion. (See Chapter IV for details.) Consequently, sets of samples coming out of the "hot-cell" were not identical. Most irradiations were carried out at 1" from the centre; a few sets were irradiated at 4" and 6".

b) Post-irradiation annealing at 100°C and 140°C followed. The change in the % conversion with time, during annealing, was determined for all samples, (Fig. 5.1. to 5.10).

The change of % conversion vs. time for unirradiated samples at 100°C and 140°C was available (H1, H10) (Figs. A and 5.1); it was therefore possible to make a comparison between the two cases.

In all cases the % conversion change during post-irradiation annealing was found to be similar to that for unirradiated samples (within experimental error). Fig. (5.10) is the only exception. An interpretation is provided in the coming chapter.

c) Occasionally, the presence of trapped free radicals was checked, using the E.S.R. technique. No free radicals were detected. (See the following chapter for details.)

5.2. Experiments starting with highly converted systems:

(See (App. I) for the analysis of (c-1) and (c-2).)

The two Monsanto supplied samples (about 93% and 98% conversion) are closely similar in molecular weights. Accordingly, if they are to be treated in a specific manner, the differences in results (if any) can be related to the difference in the residual monomer content.

a) Irradiation was carried out at room temperature, to a total dose of 0.742 M. rad. (165 rads/sec. x 75 minutes x 60). Irradiation was limited to 1" from the source's centre, and therefore, only six sample holders were available (see reactor description Chap. IV). This represented a constraint on the maximum number of samples that could be handled in each experimental run. To increase the number of experimental data for each set, two runs, each consisting of six samples (3 (c-1) and 3 (c-2)) were irradiated at the above mentioned conditions. The interval between the two runs was approximately two months, and $[R^{\bullet}_{o}]$ was measured

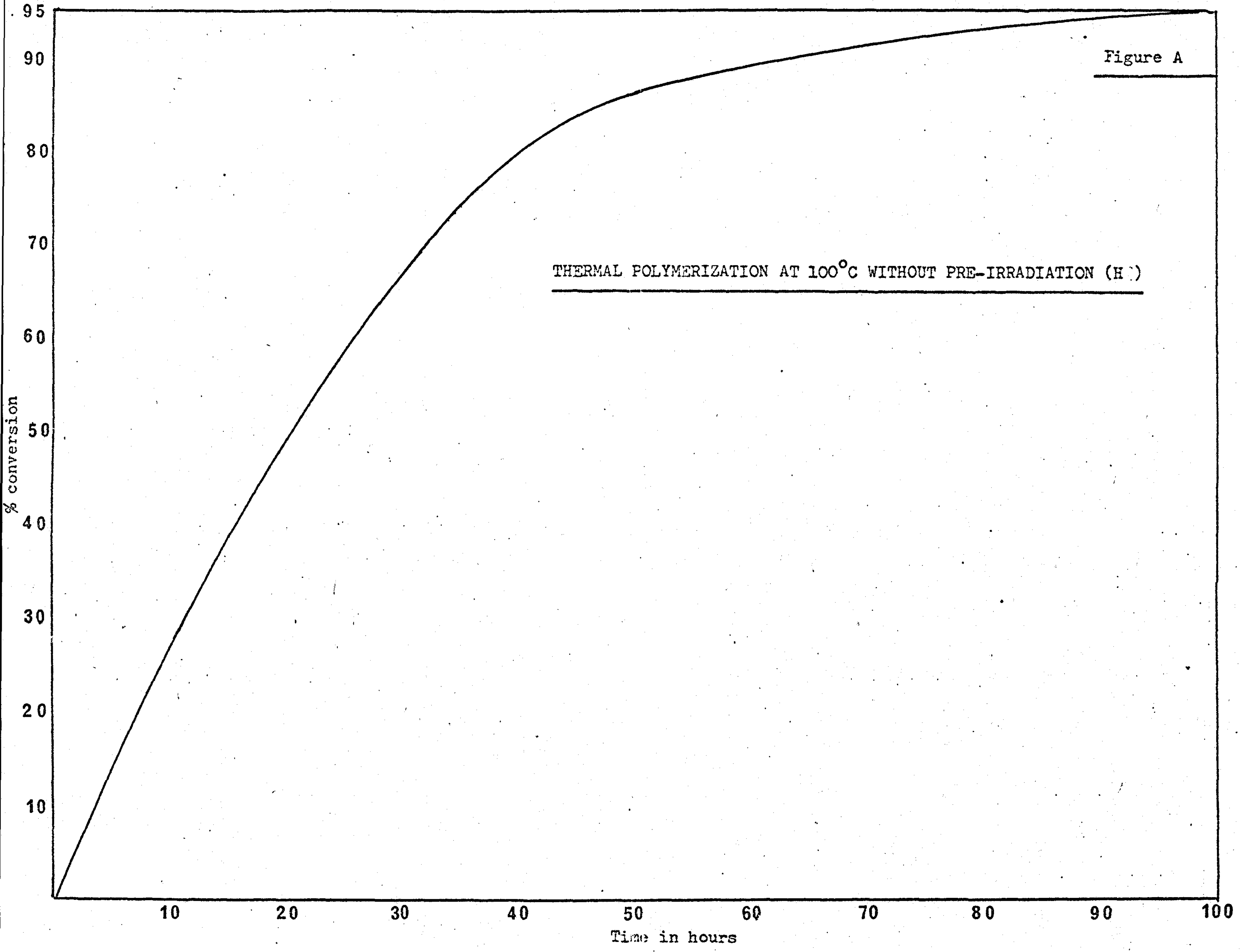
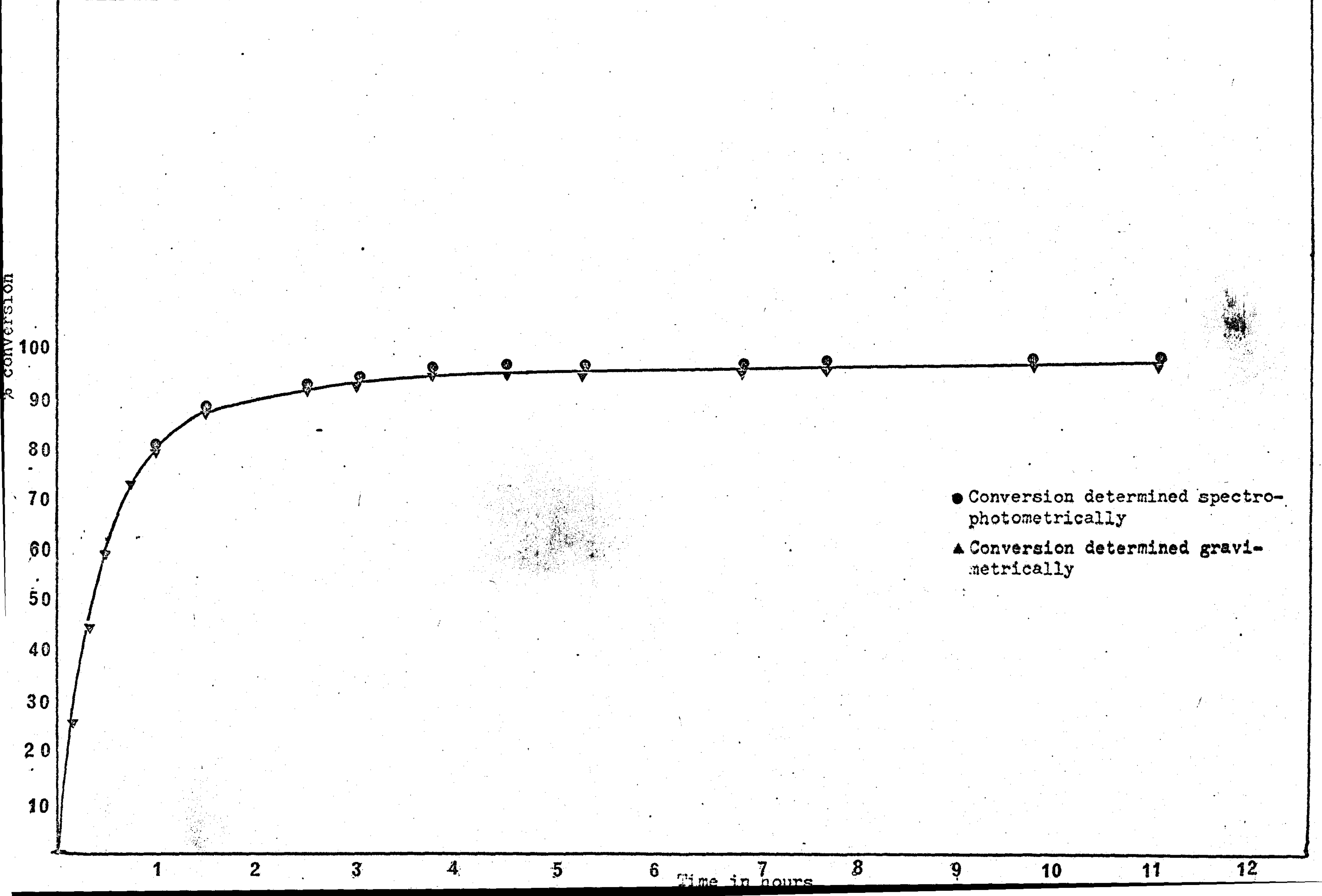


Figure A

THERMAL POLYMERIZATION AT 100°C WITHOUT PRE-IRRADIATION (H [illegible])

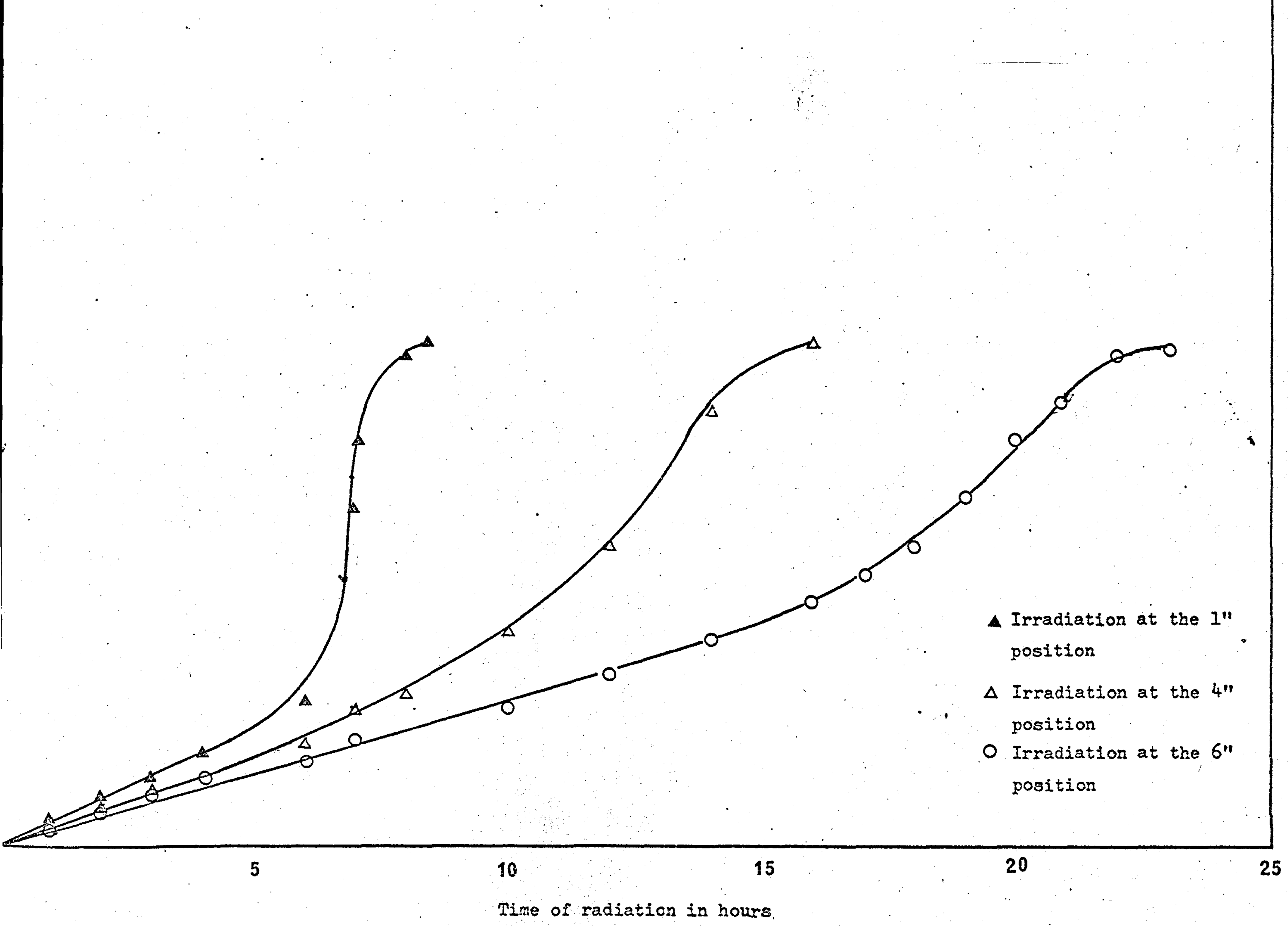
THERMAL POLYMERIZATION AT 170°C WITHOUT PRE-IRRADIATION (H13)

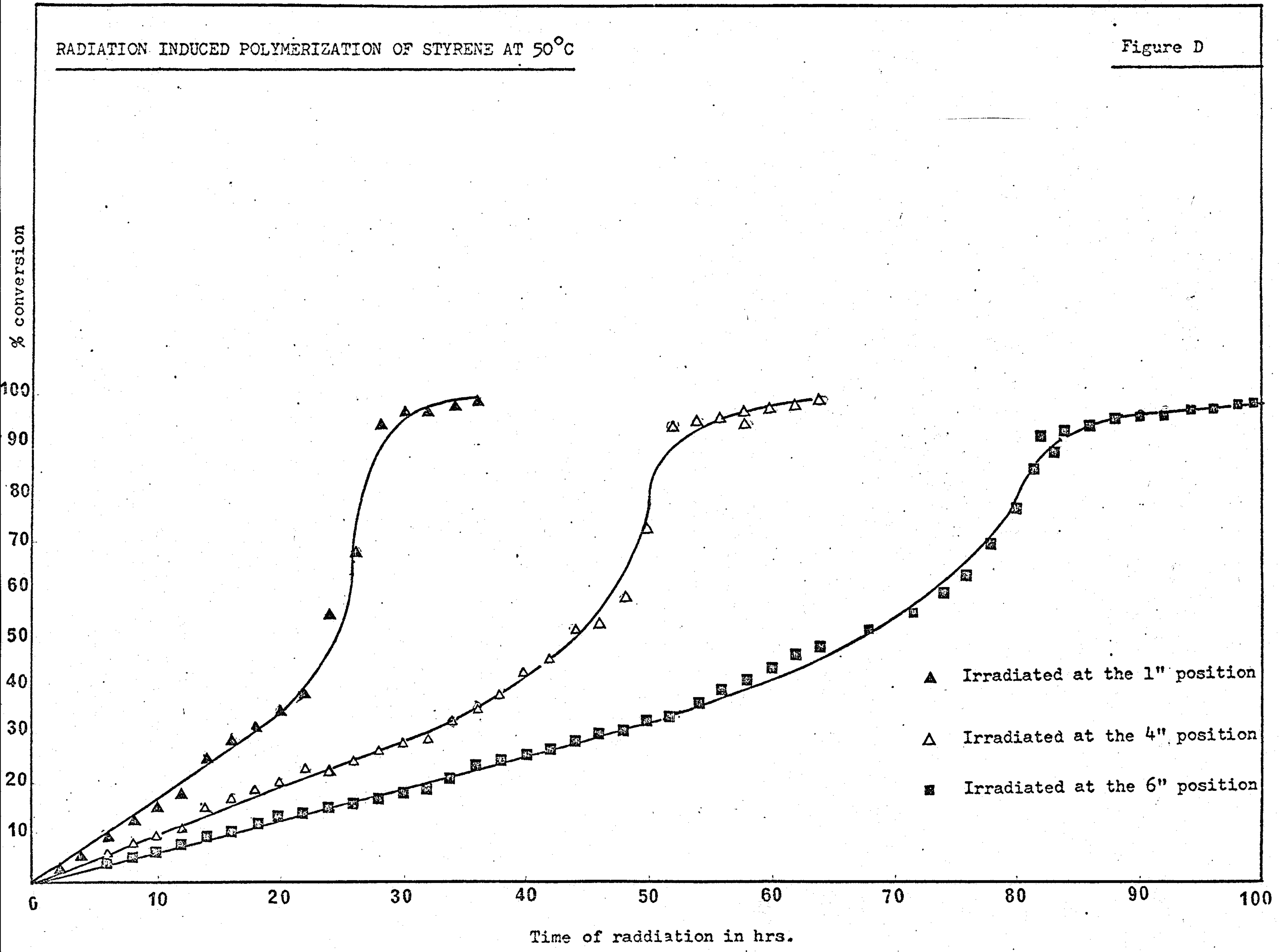
Figure B



RADIATION-INDUCED POLYMERIZATION AT 85°C (H)

Figure C



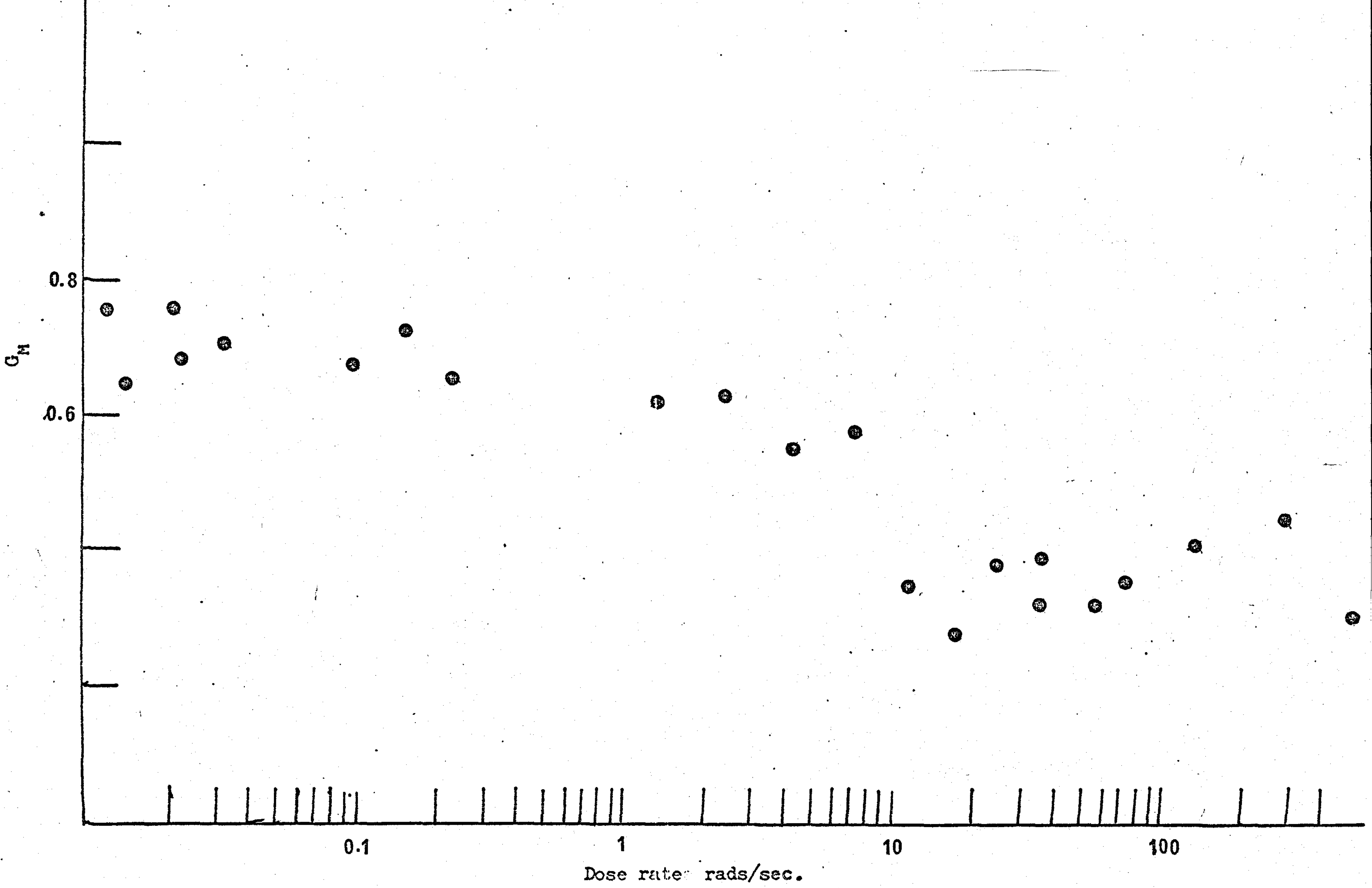


RADIATION INDUCED POLYMERIZATION OF STYRENE AT 50°C

Figure D

G_M VALUES REPORTED IN THE LITERATURE, AT DIFFERENT DOSE RATES (C4)

Figure E



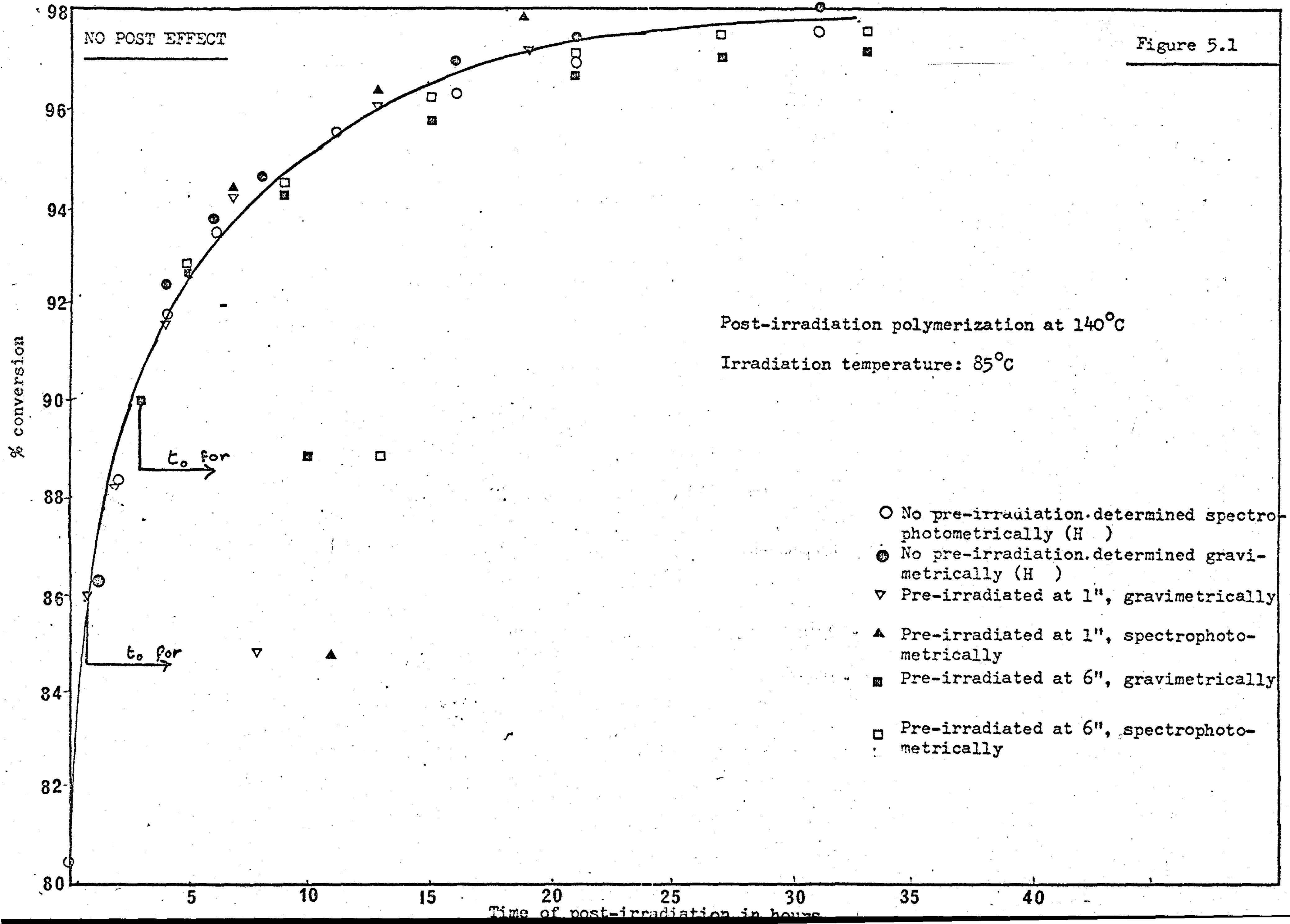

98
96
94
92
90
88
86
84
82
80
% conversion
5
10
15
20
25
30
35
40
Time of post-irradiation in hours
NO POST EFFECT
Post-irradiation polymerization at 140°C
Irradiation temperature: 85°C
t₀ for □ ▣
t₀ for ▽ ▲
○ No pre-irradiation determined spectrophotometrically (H)
● No pre-irradiation determined gravimetrically (H)
▽ Pre-irradiated at 1", gravimetrically
▲ Pre-irradiated at 1", spectrophotometrically
▣ Pre-irradiated at 6", gravimetrically
□ Pre-irradiated at 6", spectrophotometrically

Figure 5.1

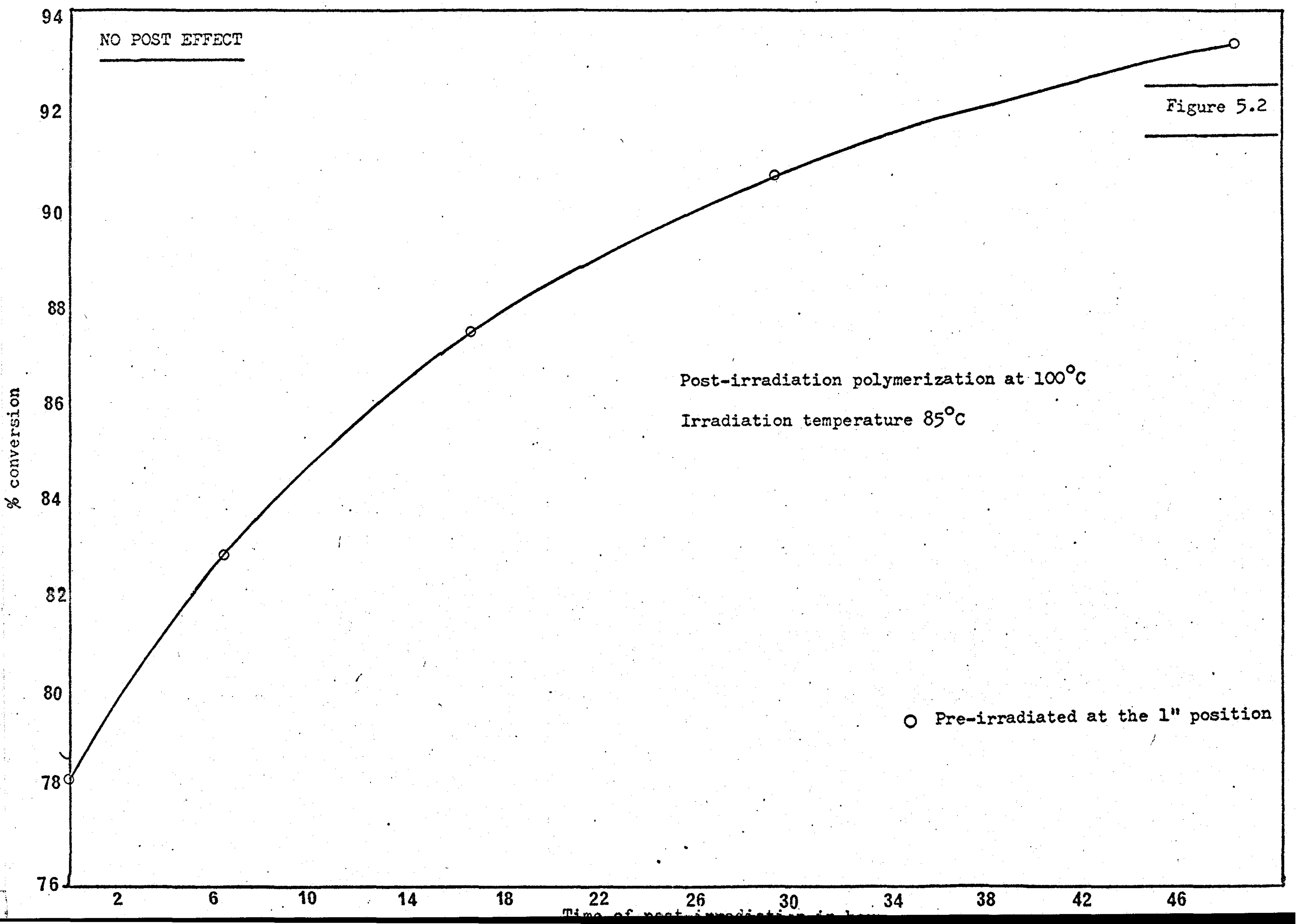

NO POST EFFECT
% conversion
94
92
90
88
86
84
82
80
78
76
2
6
10
14
18
22
26
30
34
38
42
46
Post-irradiation polymerization at 100°C
Irradiation temperature 85°C
○ Pre-irradiated at the 1" position

Figure 5.2

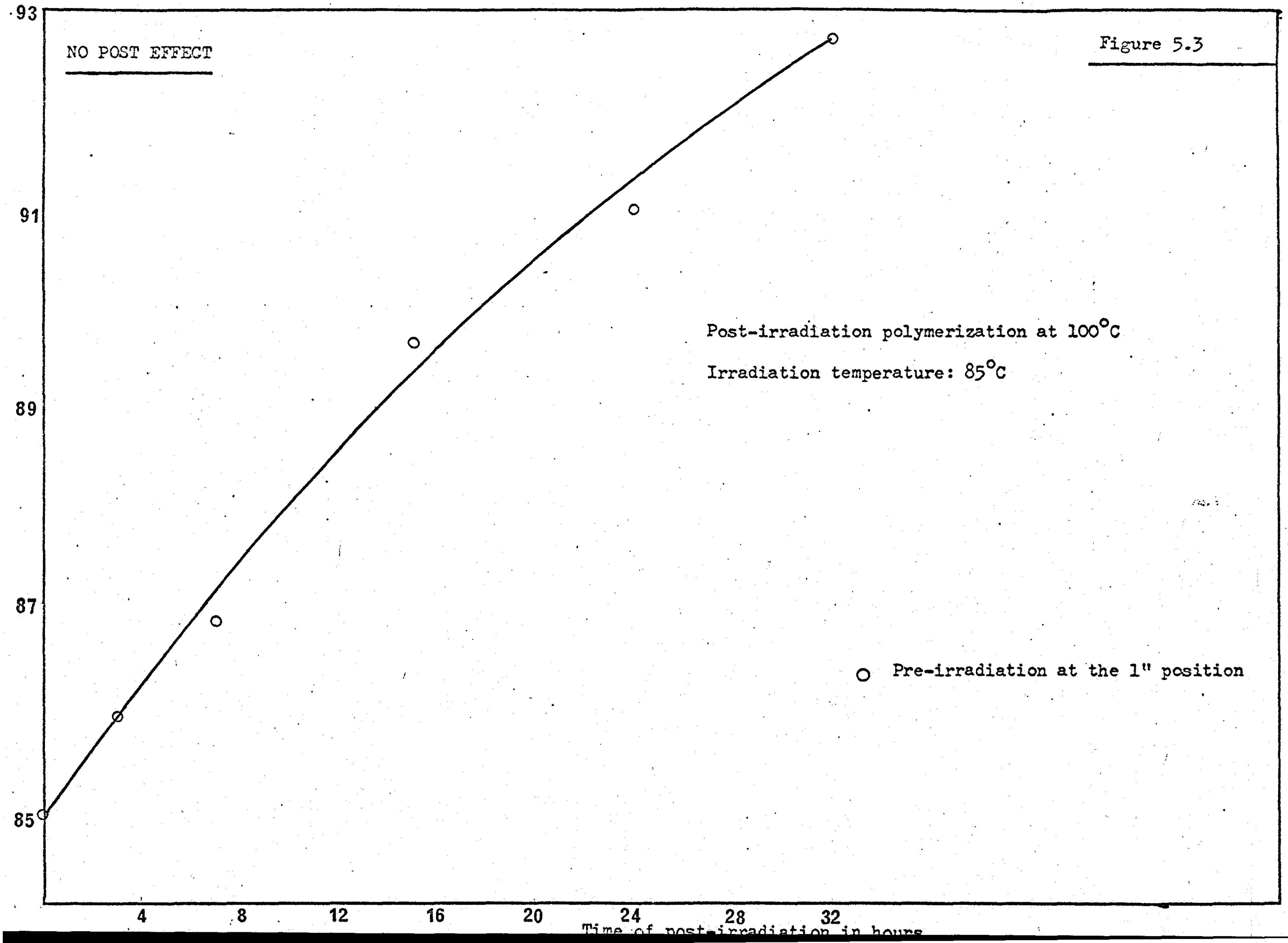


Figure 5.3

NO POST EFFECT
Post-irradiation polymerization at 100°C
Irradiation temperature: 85°C
○ Pre-irradiation at the 1" position
93
91
89
87
85
4
8
12
16
20
24
28
32
Time of post-irradiation in hours

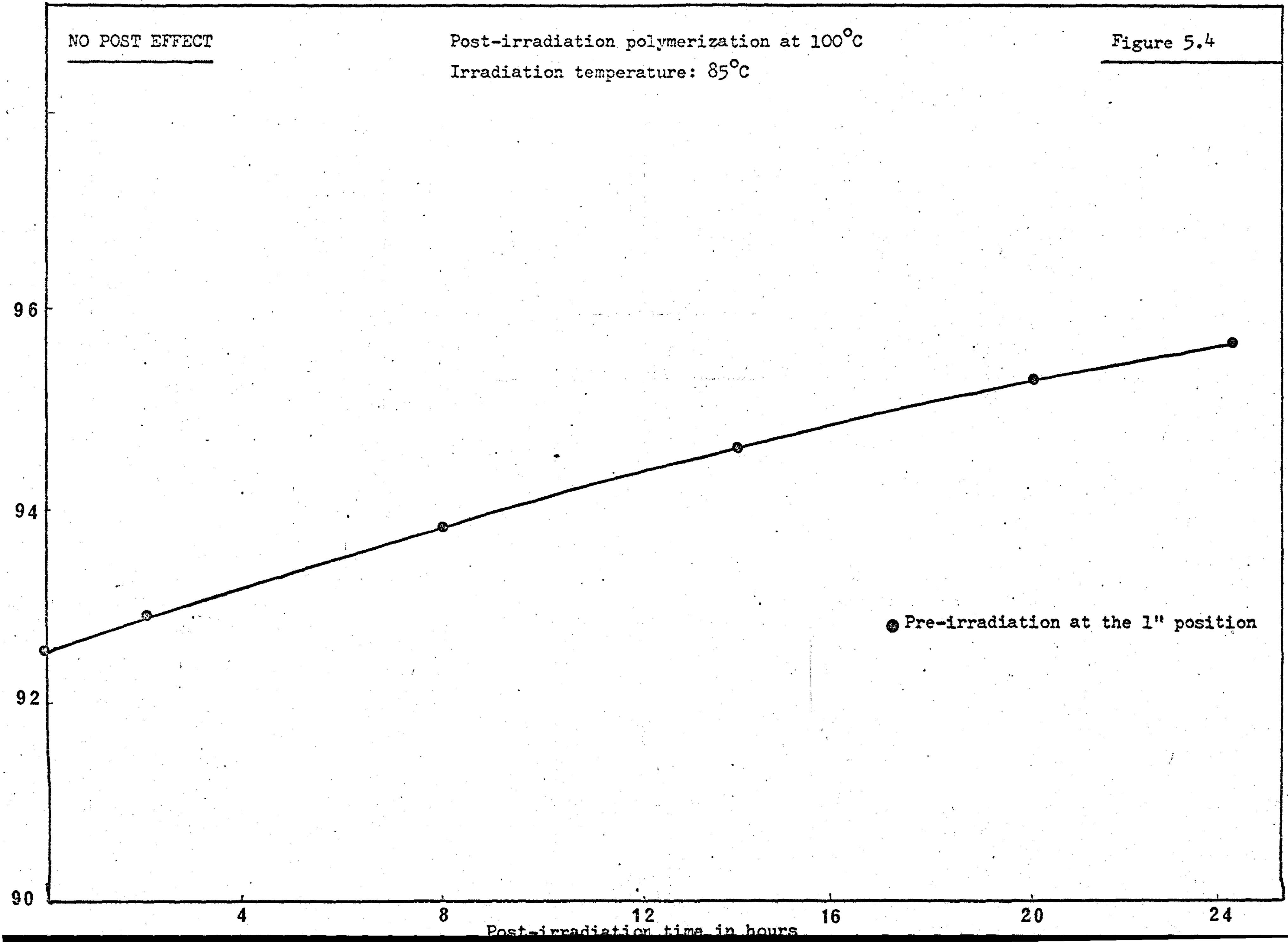


Figure 5.4

Post-irradiation polymerization at 100°C
Irradiation temperature: 85°C

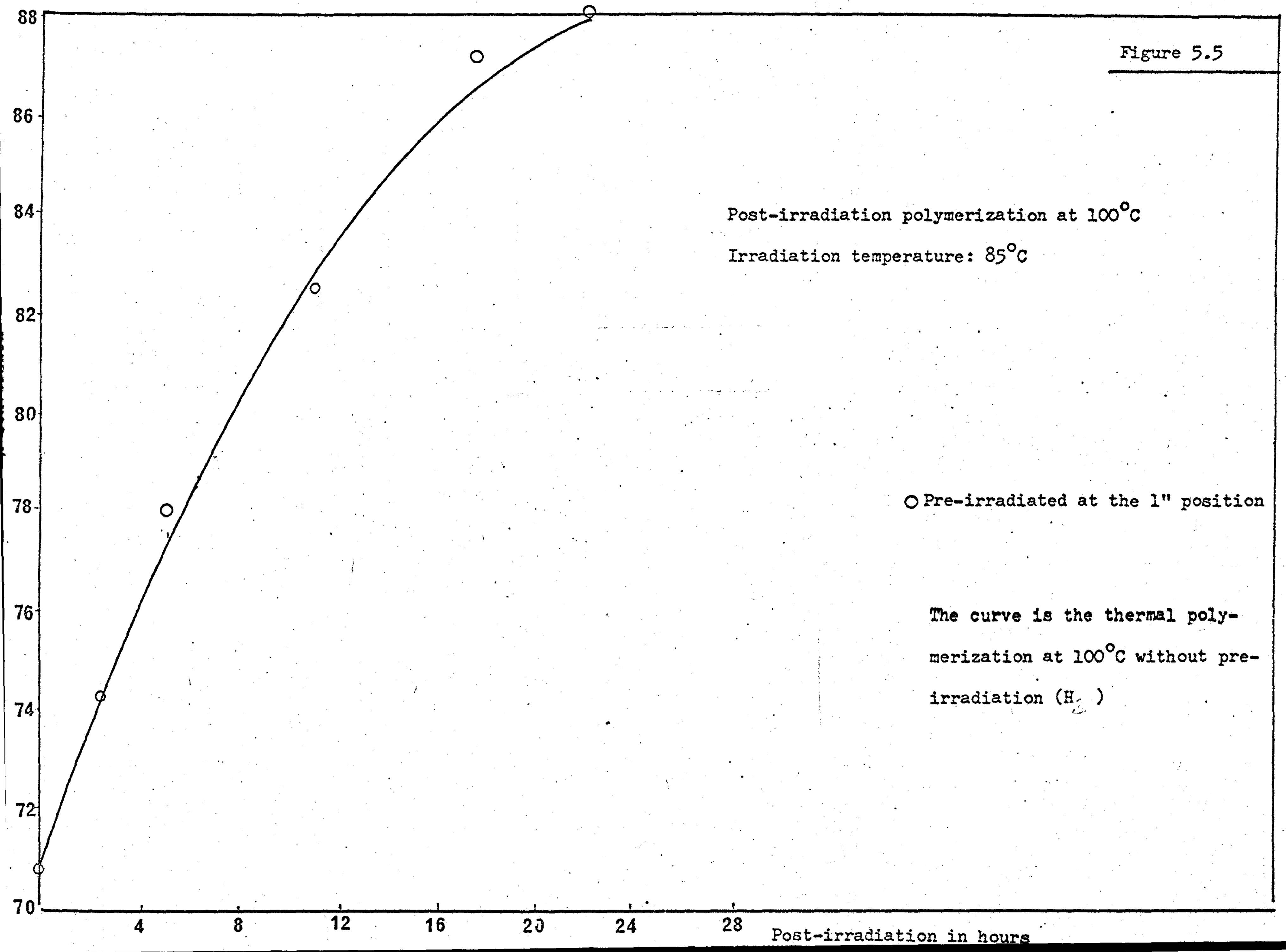


Figure 5.5

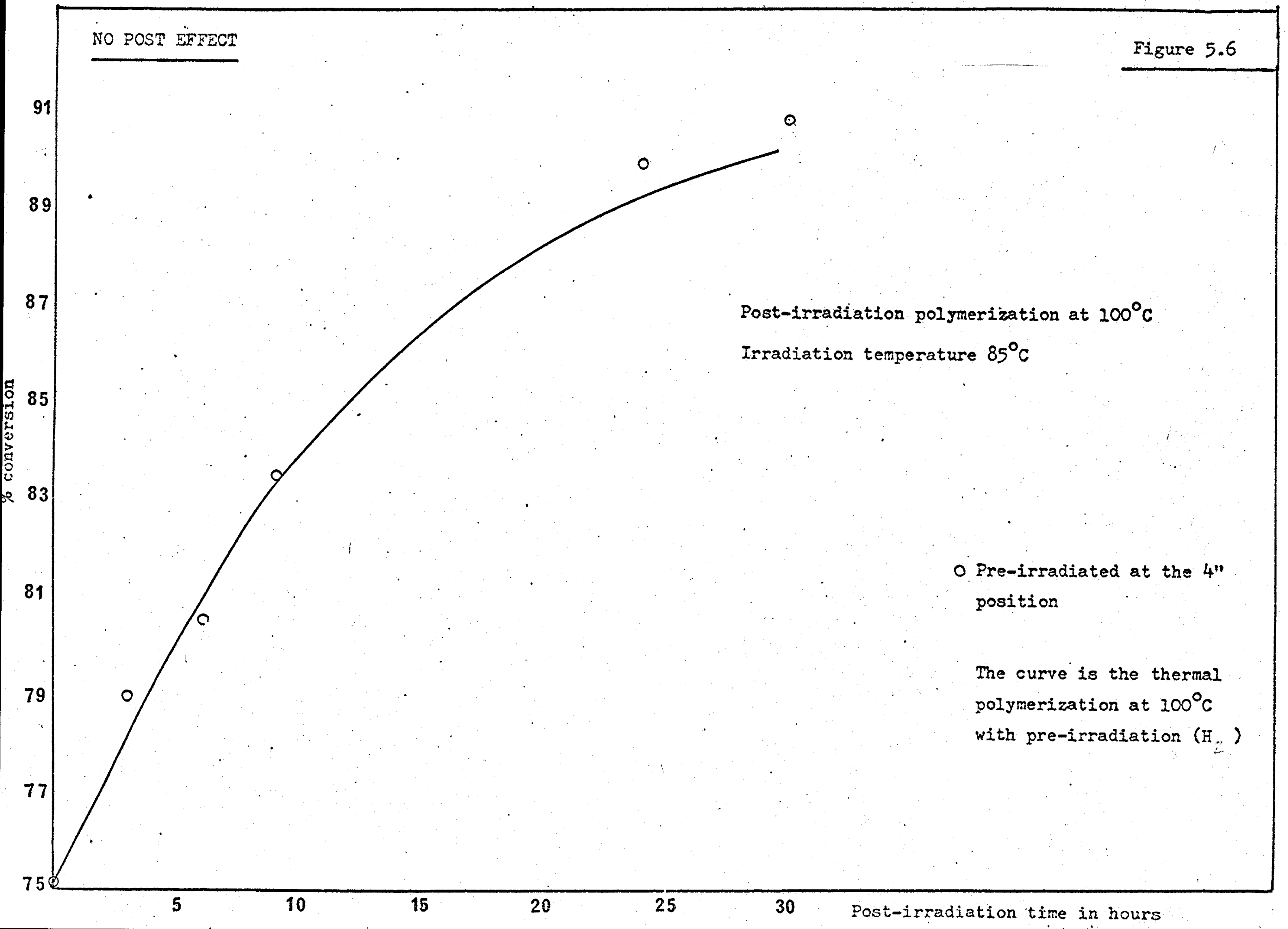
Post-irradiation polymerization at 100°C

Irradiation temperature: 85°C

○ Pre-irradiated at the 1" position

The curve is the thermal polymerization at 100°C without pre-irradiation (H)

Figure 5.6



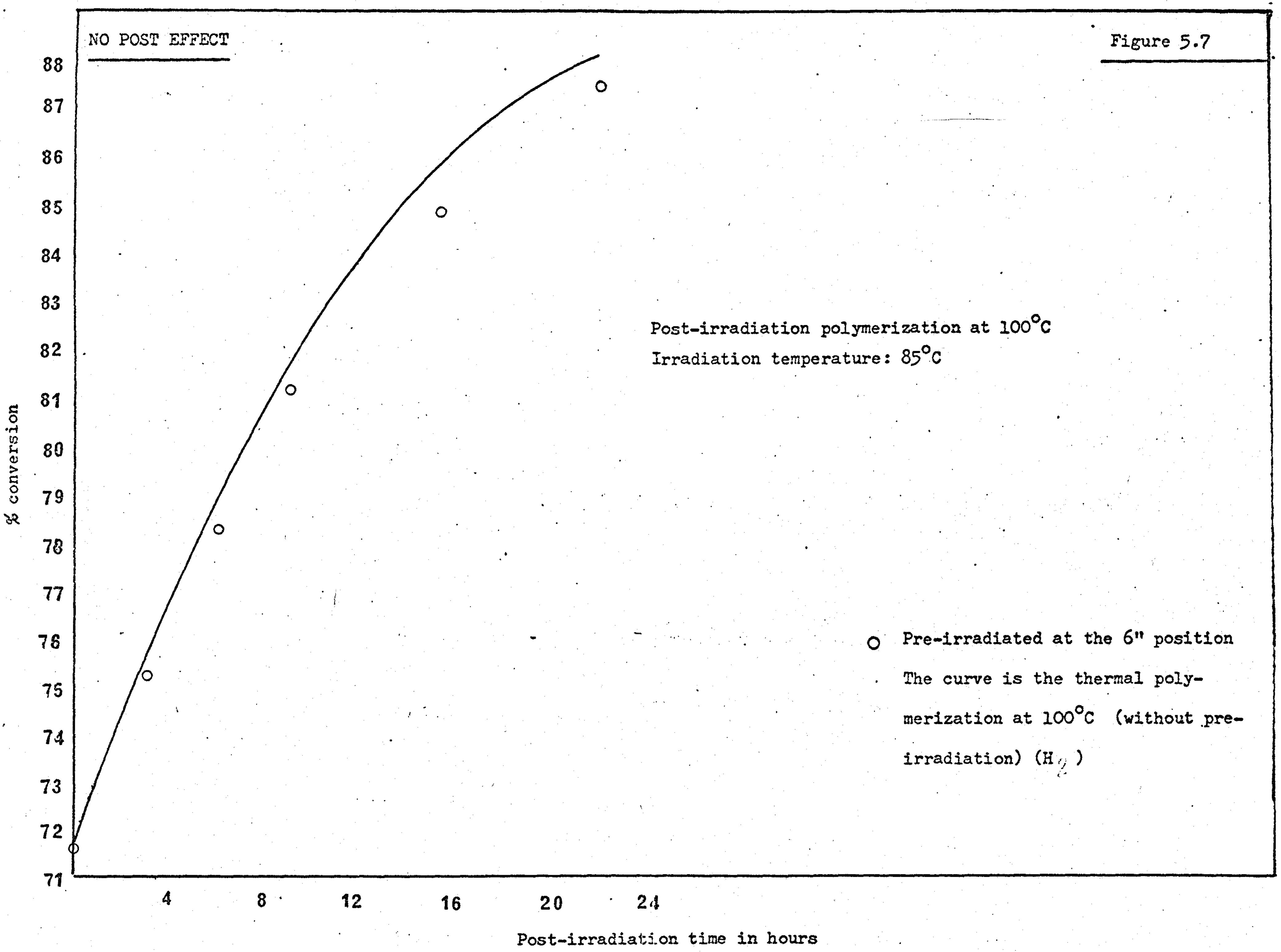
Post-irradiation polymerization at 100°C

Irradiation temperature 85°C

○ Pre-irradiated at the 4" position

The curve is the thermal polymerization at 100°C with pre-irradiation (H_2)

Figure 5.7



NO POST EFFECT

Post-irradiation polymerization at 100°C
Irradiation temperature: 85°C

○ Pre-irradiated at the 6" position
The curve is the thermal polymerization at 100°C (without pre-irradiation) (H_2)

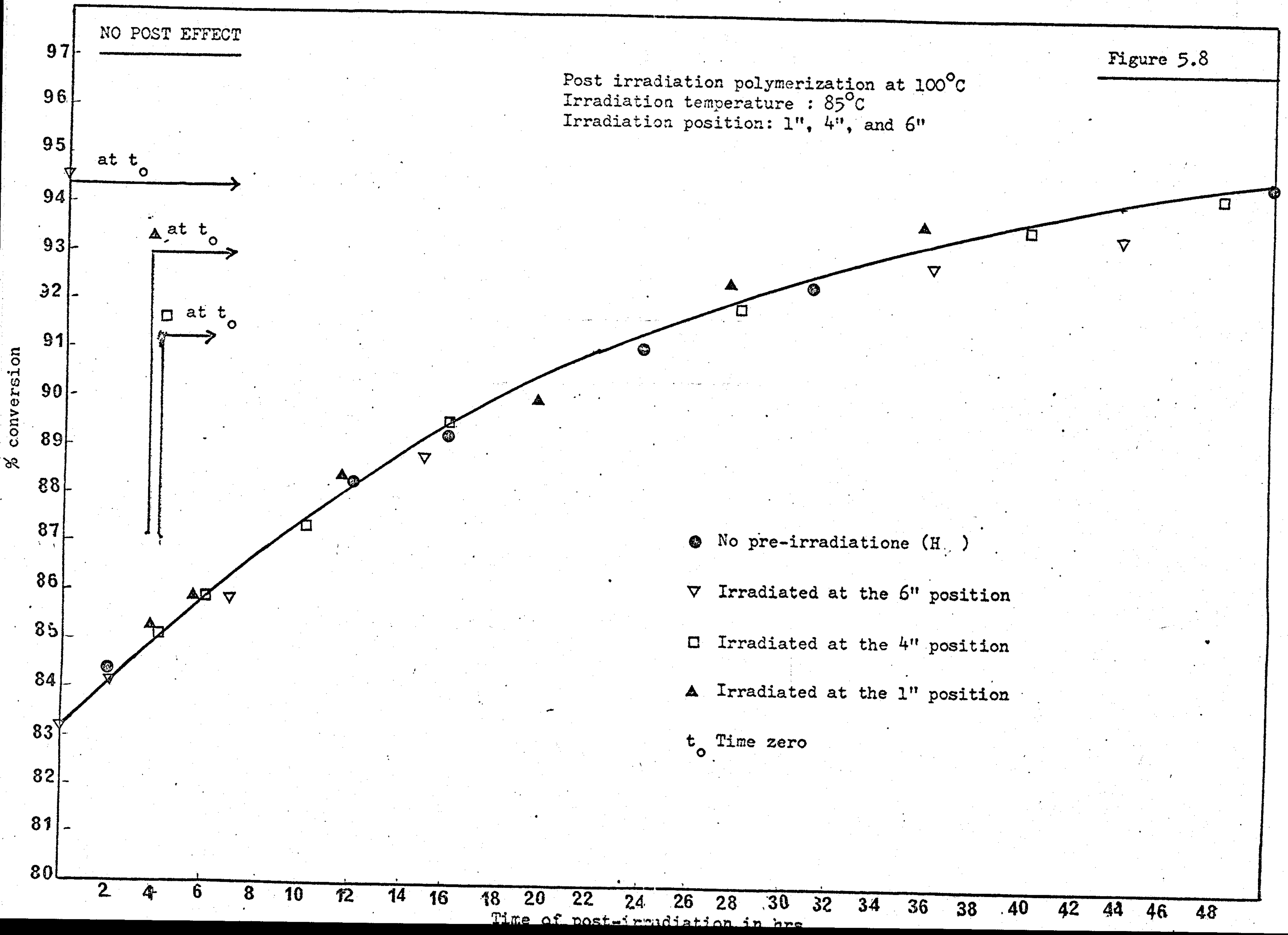


Figure 5.8

NO POST EFFECT
Post irradiation polymerization at 100°C
Irradiation temperature : 85°C
Irradiation position: 1", 4", and 6"
at t_o
at t_o
at t_o
% conversion
97
96
95
94
93
92
91
90
89
88
87
86
85
84
83
82
81
80
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
Time of post-irradiation in hrs
● No pre-irradiatione (H)
▽ Irradiated at the 6" position
☐ Irradiated at the 4" position
▲ Irradiated at the 1" position
t_o Time zero

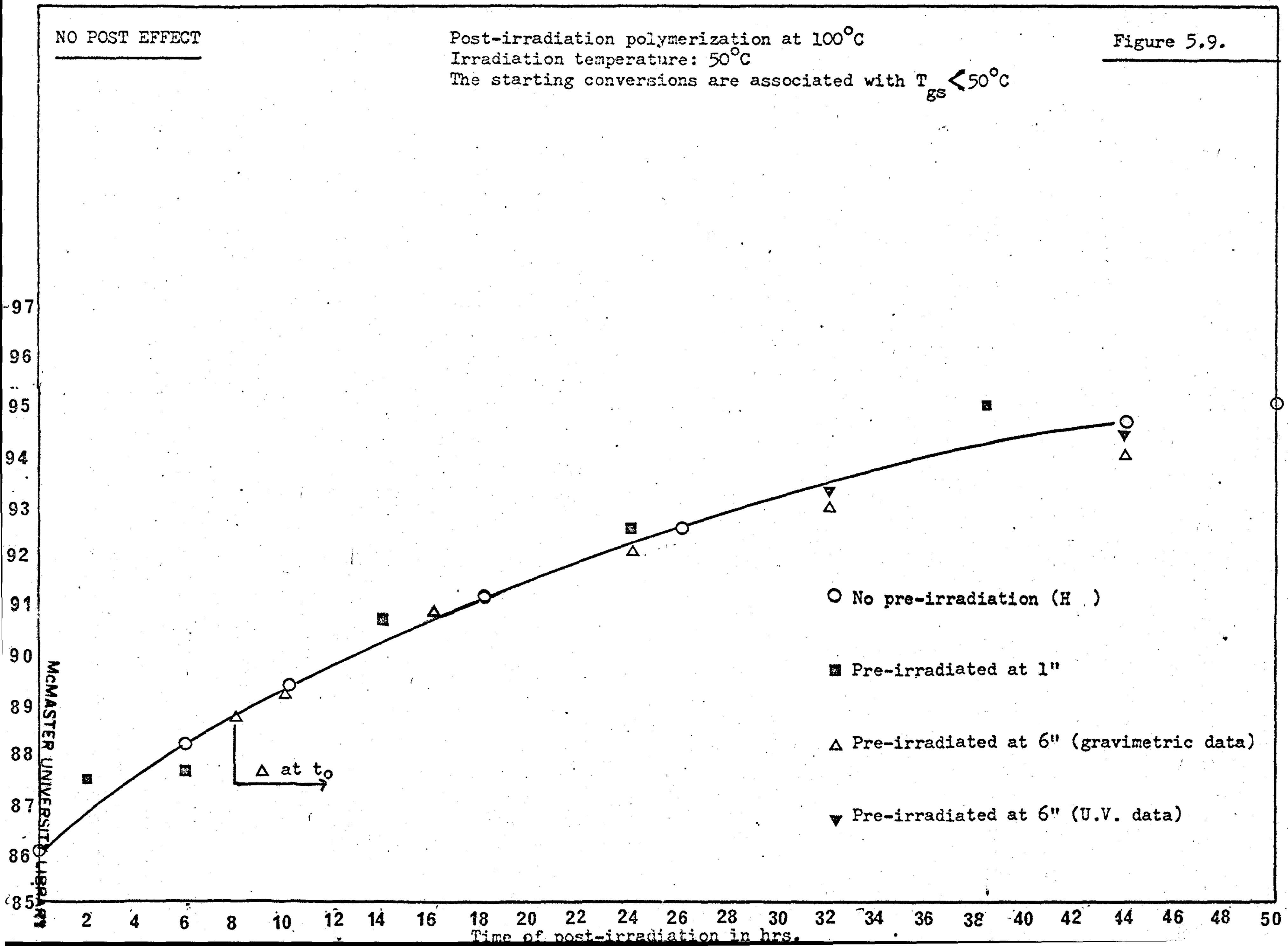


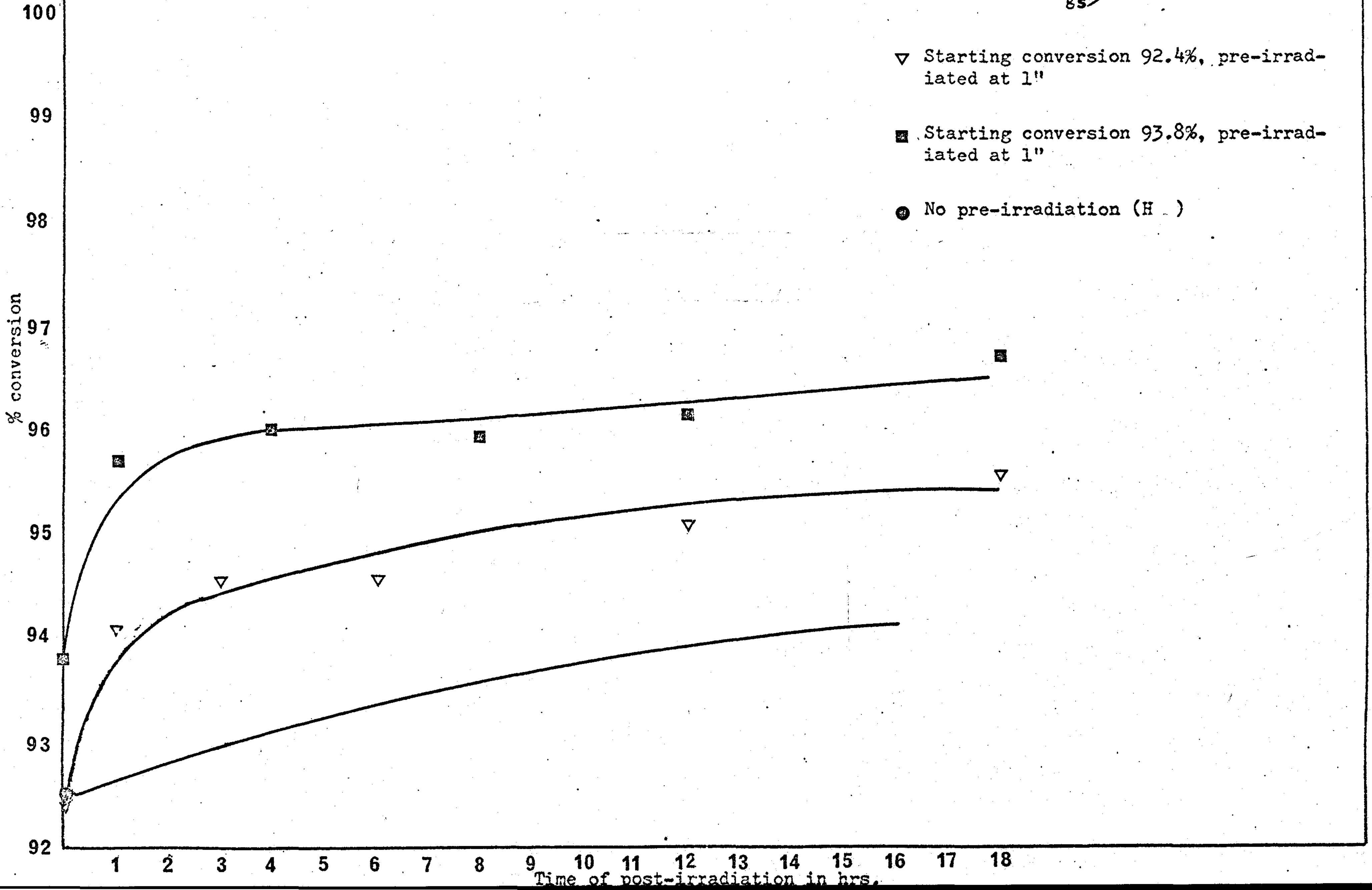
Figure 5.9.

Post-irradiation polymerization at 100°C
Irradiation temperature: 50°C
The starting conversions are associated with $T_{gs} < 50°C$

POSITIVE EVIDENCE OF POST EFFECT

Post-irradiation polymerization at 100°C
Irradiation temperature: 50°C
The starting conversions are associated with $T_{gs} > 50°C$

Figure 5.10



for every sample; consequently there was no need to reserve a sample for $[R^{\bullet}_{o}]$ determination in every set where $[R^{\bullet}_{o}]$ is defined by "the free radical concentration immediately after irradiation." $[R^{\bullet}_{o}]$ was found to be constant throughout the investigation. The measured values of $[R^{\bullet}_{o}]$ are given in (tables 6.1 and 6.2). The % conversion did not change by irradiating under the above mentioned conditions. Accordingly, all (c-1) sets were identical immediately after the irradiation treatment (free radical concentration, % conversion, molecular weight). The same applies to(c-2) sets.

b) Post-irradiation annealing at varied temperatures, above and below T_{gs}, followed. Every set of samples was treated as described on (page).

The three experimental measurements ($[R^{\bullet}]$, % conversion and M_n) have been executed to clarify the behaviour of trapped radicals in relation to temperature, their effect in promoting post-irradiation polymerization, and their influence over M_n. Values of $[R^{\bullet}]$, (the free radical concentration at any time), are given in:

i) Table (6.1.) for (c-1) samples, annealed at temperatures below T_{gs}.
   Fig. (6.1) shows $[R^{\bullet}]$ vs. time at temperatures less than T_{gs}, and Fig. (6.1) is the corresponding plot of $1/[R^{\bullet}]$ vs. time.

ii) Tables (6.2a) and (6.2b) for (c-2) samples, annealed at temperatures, below and above T_{gs2}, respectively.
   Figs. (6.2a) and (6.2b) are the corresponding $R^{\bullet}$ vs. time plot; and Figs. (6.2a) and (6.2b) are those of the corresponding $1/[R^{\bullet}]$ vs. time.

The change in the % conversion with time, at varied post-irradiation annealing temperatures is given in: Fig. (6.3) and Fig. (6.4) for (c-1) and (c-2), respectively.

Figs. (6.5) and (6.6) represent the change in the % conversion with time at 100°C and 170°C for (c-1), without pre-irradiation.

Finally, M_n was measured for 3 sets of samples, and the results are given in Table (6.4).

5.3. The Glass Transition Temperature of Styrene - Polystyrene Systems (T_{gs})

For free radicals to be trapped in high concentration in a pure polymer, the latter must be in the glassy state (see Chapter II). It is therefore logical to assume that the same applies to polymer-monomer systems.

T_{gs}, the glass transition temperature of the system, is a function of the polymer to monomer ratio. Kelly and Bueche (K.4) derived a model which gives T_{gs} as a function of conversion. (For the theoretical derivation of T_{gs} and T_{gs2} for (c-1) and (c-2), respectively, see App. 9.)

Knowing T_{gs1}, and T_{gs2} helped in selecting the necessary irradiation temperature. Annealing temperatures were chosen to be evenly distributed above and below T_{gs}.

CHAPTER VI

Results, Assumptions and Discussion

This chapter is divided into two parts. The first part outlines the results obtained by starting with pure monomer. These could only be analysed qualitatively, and their discussion immediately follows the results presentation.

The second part, is concerned with the results obtained by starting with the two highly converted solid samples (c-1) and (c-2). Quantitative deductions are presented. The results are grouped in point form. Their discussion follows in another section, together with the assumptions made.

6.1. Experiments starting with pure monomer:

6.1.1. Irradiation at 85°C:

a) Results:

Attempts to stop the radiation induced reaction at a pre-determined conversion were not successful. Consequently, annealing was performed on "sets of samples" which possess different % conversion i.e. non-identical sets.

Electron Spin Resonance measurements were conducted on several samples; none yielded a detectable concentration of free radicals.

Irradiation was mainly at 1" from the centre. Post-irradiation annealing was at 100°C in most cases. Figures (5.2 and 5.8) show plots of conversion vs. time. No 2 "sample sets" possessed the same conversion at the start of annealing. However, it was interesting to note that variation of conversion with time, during annealing, had more or less a similar pattern in all cases. It was also comparable to the rate of polymerization of unirradiated samples (in the same conversion region). i.e. It did not show a post-effect. In Figure (5.1) which represents post-irradiation annealing at 140°C, no post-effect was noticed either.

b) Discussion:

Failing to detect any trapped radicals by the Electron Spin Resonance Spectrometer, might indicate a concurrent production and decay of free radicals, the decay being fast enough to prevent the accumulation of large concentrations of free radicals. The rapid rates of decay can be explained by the fact that, irradiation was always carried out in the rubbery state i.e. at temperatures above T_{gs} (see the theoretically estimated T_{gs} (App.9), for % conversions at which the radiation induced reactions were stopped). The absence of the post-effect, is attributed to the failure in trapping radicals, which if present, would have promoted rapid polymerization rates.

Different dose rates during irradiation are expected to yield "sample sets" with different molecular weight characteristics. Consequently, the similarity of post-irradiation polymerization patterns is somewhat surprising (see Figure 5.8).

6.1.2. Irradiation at 50°C:

a) Results:

The radiation induced polymeriation of styrene took place at 50°C. It was followed by post-irradiation annealing at 100°C. (Figure 5.9) illustrates the change of conversion with time, during the annealing of two sets, removed from the radiation field at 86% and 88.8% conversion. Similarly, (Figure 5.10) illustrates two sets removed at 92.4% and 93.8% conversion. No post-effect was observed in (Figure 5.9). However, (Figure

5.10) shows a post-effect, illustrated by the high initial polymerization rate.

b) Discussion:

For the two sets shown on (Figure 5.9), the radiation was stopped while the % conversion of the systems corresponded to (T_{gs}) lower than the radiation temperature 50°C (see T_{gs} for 86% and 88.8% conversion, in App. 9).

Accordingly, radicals were being formed in rubbery media, and their decay is expected to be very rapid during the course of their fromation. This explains why no post-effect was observed during annealing. (Figure 5.10) differs from (Figure 5.9), in that radiation was stopped after the systems were transformed to the glassy state (see T_{gs} for 92.4% and 93.8% conversion), thus enabling some free radicals to be trapped. This explains the observed rapid initial polymerization rates during annealing.

6.2. Starting with highly converted systems ((c-1) and (c-2)):

Irradiation was limited to a fixed total dose of 0.742 M rad., at the 1" positions. It was carried out at room temperature, where both systems are well below their T_{gs} (see App. 9, T_{gs} at 92.95 and 98% conversion), thus allowing high concentrations of free radicals to be trapped. In addition, no polymerization took place during irradiation. It was therefore possible, to obtain several identical sample sets of either (c-1) or (c-2), immediately after irradiation.

A quantitative treatment of the changes taking place during post-irradiation annealing, was performed. The following topics were investigated:

a) G-values, of the polymer and monomer.

b) Order of termination reaction.

c) Rate constants of free radicals' termination reaction as a function of temperature.

d) Activation energies of decay, below and above T_{gs}.

e) Variation of number average molecular weights with the progress of post-irradiation polymerization

f) The chemical structure of the trapped radicals.

g) Change of % conversion with time, during annealing, at varied temperatures.

Experimental and theoretical results are to be introduced in the following order:

1. Results summary.
2. Calculations and assumptions used in obtaining the results and their discussion.

6.2.1. Results summary:

6.2.1a. G-values:

The $G_{p^{\cdot}}$ i.e. that of entrapped polymer free radicals.

$$= 0.43 \pm 50\%$$

$$= 0.215 \pm 50\% \quad (\text{assuming } G_{M^{\cdot}} = \tfrac{1}{2} G_{p^{\cdot}})$$

6.2.1b. Free radicals' decay, order, and mechanism:

Free radicals' decay rate is a fairly good "second order" at all investigated temperatures, and at both the rubbery and glass states and for both (c-1) and (c-2) samples. This could be represented by:

$$1/[R^{\cdot}] - 1/[R^{\cdot}_{o}] = Kt$$

Free Radicals Decay Data

A (c-1) sample

Replicates at time zero:

$$[R^{\cdot}_{o}] = (19.0,\ 19.0,\ 19.1,\ 19.3,\ 18.9,\ 18.8) \times 10^{16} \approx 19 \times 10^{16}\ \text{F.R/gm}$$

Table (6.1)

Temp. °C	R F.R/gm x 10^{-16}	1/R· gm/F.R.x 10^{+17}	t (hrs)
22.5 ± 1.5	17.7	0.565	50
	15.1	0.663	100
	13.7	0.730	200
	11.5	0.870	300
	10.1	0.990	400
	9.3	1.075	500
40.0 ± 1	17.2	0.581	4
	17.2	0.581	8
	15.8	0.633	12
	15.4	0.649	16
	14.1	0.709	20
	13.1	0.763	24
50.0 ± 1	17.8	0.562	2
	15.5	0.645	4
	15.2	0.658	6
	13.5	0.741	8
	12.7	0.787	10
	12.5	0.8	12

B (c-2) sample

Replicates at time zero:

$$\left[R^{\cdot}_{o}\right] = (20, 20, 20.1, 20.4, 19.8, 19.7)\times 10^{16} = 20 \times 10^{16} \text{ F.R/gm}$$

Table (6.2.a)

For $T < T_{gs}$

Temp. °C	$R^{\cdot}$ F.R/gm x 10^{-17}	$1/R^{\cdot}$ gm/F.R x 10^{+17}	t (hrs.)
22.5 ± 1.5	1.87	0.535	50
	1.66	0.602	100
	1.45	0.690	200
	1.31	0.763	300
	1.19	0.840	400
	1.06	0.943	500
50.0 ± 1	1.79	0.559	2
	1.68	0.595	4
	1.62	0.617	6
	1.52	0.658	8
	1.38	0.725	10
	1.32	0.758	12
70.0 ± 1	1.35	0.741	1
	1.13	0.885	2
	0.88	1.136	3
	0.78	1.282	4
	0.66	1.515	5
	0.58	1.7241	6

For T> T_{gs}

Table (6.2.b)

Temp. °C	R' F.R/gm x 10^{-17}	1/R' gm/F.r x 10^{17}	t minutes
100.2 ± 1.2	0.81	1.234	10
	0.65	1.538	15
	0.46	2.174	25
	0.33	3.030	35
	0.28	3.571	45
	0.21	4.762	60
110.4 ± 1.2	0.372	2.688	10
	0.218	4.587	20
	0.144	6.944	30
	0.115	8.696	40
	0.093	10.753	50
	0.074	13.514	60
120.5 ± 1.3	0.134	7.463	10
	0.115	8.696	12.5
	0.092	10.870	15
	0.073	13.699	20
	0.059	16.949	25
	0.048	20.833	30

6.2.1c. Rate constants of decay:

Calculated rate constants of the termination reaction at different temperatures are listed below within 95% confidence limits:

Activation Energies for Decay

Table (6.3)

T^o c	K_t ml/mole. sec.	E K cal/mole
22.5 ± 1.5	1.39 ± 0.05	
50.0 ± 1	33.60 ± 2.28	22.9 ± 1.7
70 ± 1	319.74 ± 9.10	
100.2 ± 1.2	6.663×10^3 ± 148	
110.4 ± 1.2	20.027×10^3 ± 500	32 ± 1.0
120.5 ± 1.3	63.527×10^3 ± 1143	
22.5 ± 1.5	1.78 ± 0.08	
40 ± 1	14.57 ± 1.54	21.4 ± 1.1
50.0 ± 1	39.13 ± 3.43	

(Figure 6.1) is a plot of free radical concentration vs. time at temperatures below (T_{gs}) (for (c-1) sample). (Figure 6.1') shows the best fit obtained when plotting 1/ R• vs. time. (Figures 6.2.a and 6.2.a') are the same as (6.1) and (6.1') but applied to (c-2) sample at T below T_{gs}. (Figures 6.2.b and 6.2.b') are plotted in a similar way, for (c-2) sample, at temperature above T_{gs}.

6.2.1d Activation energies:

The calculated activation energies for the decay reaction above and below (T_{gs}) for (c-2) samples, and below (T_{gs}) for (c-1), are listed in the table on the previous page.

(Figures 6.1" and 6.2") show best fits obtained by the least squares technique (see App. VII) as applied to Arrhenius relation for (c-1) and (c-2) samples.

6.2.1e. Molecular weights:

The number average molecular weights for three sample sets determined by osmometry are listed below along with the corresponding % conversions and annealing temperatures.

Number Average Molecular Weight Data

Table (6.4)

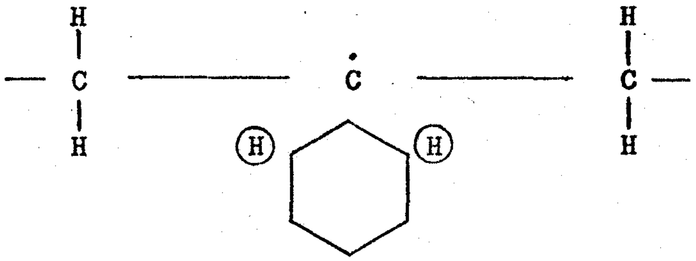
Sample	Temp. °C	Time min.	% Conv.	$Mn \times 10^{-3}$
c-1	172	0	92.95	126.6*
c-1	172	10	98.12	130.0
c-1	172	15	98.39	126.0
c-1	172	20	98.94	131.6
c-1	172	25	00.06	120.0
c-1	172	30	98.82	120.8
c-1	172	40	98.90	124.9
c-1	100.5	0	92.95	126.6*
c-1	100.5	10	95.40	128.7
c-1	100.5	15	96.12	130.0
c-1	100.5	20	97.58	118.4
c-1	100.5	30	97.73	126.0
c-1	100.5	45	97.61	123.3
c-1	100.5	60	97.70	120.0
c-2	100.2	0	98.00	120.0*
c-2	100.2	10	98.48	121.8
c-2	100.2	15	98.57	126.0
c-2	100.2	25	99.29	116.0
c-2	100.2	35	99.24	113.9
c-2	100.2	45	99.35	127.0
c-2	100.2	60	99.35	118.4

* The M_n given by Monsanto are: 126.6×10^3 and 120.0×10^3 for (c-1) and (c-2), respectively. Three (c-1), and three (c-2) samples were tested prior to and after irradiation, and M_n values fluctuated around the values given by Monsanto. i.e. effect of radiation was (-) ve, or in other words, the sensitivity of the Osmometer could not detect the small change in M_n (if any).

6.2.1f. Free Radical Structure:

The Electron Spin Resonance Spectrometer yielded a signal corresponding to the first derivative of absorption with respect to the magnetic field.

The signal's shape obtained in this investigation resembles that obtained by Ref. (F.1), who attributed it to a free radical of the structure:



with the principal hyperfine interaction with the two ring hydrogens in the ortho positions.

6.2.1g. Post-Irradiation Polymerization:

(Figures 6.3 and 6.4) represent plots of % conversion vs. time at varied annealing temperatures for (c-2) and (c-1) samples, respectively. It is clear that initial rates of polymerization are high, indicating a positive post-effect. (Figures 6.5 and 6.6) show the annealing treatment executed without pre-irradiation, for purposes of comparison.

6.2.2. Calculation, Assumptions and related Theoretical Aspects, followed by Discussion of Results:

6.2.2a. $G_{R^{\cdot}}$ values:

i) Related theoretical aspects: The definition of the G-value preceded (Chapter II). Different values of G were often reported in the literature for the same polymer, (see section 2.12.3). They presumably resulted from differences in:

- Means of free radical trapping.
- Conditions under which they were formed.
- Conditions under which E.S.R. measurements were executed.
- The presence or absence of air.

In the case at hand, polymer free radicals were formed as well as monomer free radicals. Their G-values are probably different. Chapiro (C.4) estimates $G_{M^{\cdot}}$ for styrene to be $= \frac{1}{2}\, G_{P^{\cdot}}$ for polystyrene. The theoretical ground upon which this relation is based, is given in detail in (Chapter II). Dean (D.1) is of the opinion that they are almost equal.

Another point of importance is the effect of gamma radiation on polystyrene. Two possibilities are obvious:

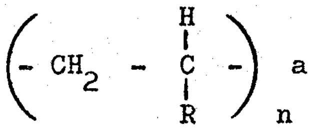
a) Chain sission (degrading polymers).

b) Cross linking (cross linking polymers).

several polymers exhibit an intermediate behaviour.

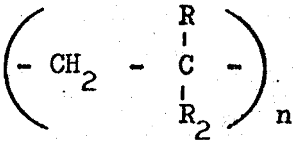
Numerous theories attempted to interpret why polymers fall into those two categories, but none appear to be entirely satisfactory. An empirical rule of thumb exists:

polymers having the structure



$\left(-CH_2 - \overset{\displaystyle H}{\underset{\displaystyle R}{C}} - \right)_n$

are cross linking polymers

whereas, those having the structure  $\left(- CH_2 - \overset{R}{\underset{R_2}{C}} - \right)_n$ are degrading polymers.

Accordingly, polystyrene is a cross linking polymer.

ii) G-values calculation: (c-1) and (c-2) chemical analysis is given in (App. I). If:

N = Avogadro's number = 6.023×10^{23}

M_{st} = Molecular weight of styrene monomer = 104.14

Therefore, the number of styrene molecules in 1 gm. pure styrene:

$$= \frac{N}{M_{st}} = 5.8 \times 10^{21}$$

a) Calculations as applied to (c-2)

(See App. I for analysis.)

1 gm. of (c-2) contains:

$5.8 \times 10^{21} \times 0.02 = 1.16 \times 10^{20}$ monomer molecules/gm sample

$\frac{N}{M_{P2}} \times 0.98 = 5 \times 10^{18}$ polymer molecules/gm sample

Where M_{P2} is the polymer molecular weight (see App. I).

Total absorbed dose:

$$D_t = \text{rads/sec.} \times \text{time in minutes} \times 60$$

$$D_t = 165 \times 75 \times 60 \simeq 0.742 \text{ M rad}$$

$$= 4.63 \times 10^{19} \text{ e.v/gm}$$

(see App. II)

The experimentally determined free radicals' concentration immediately after radiation: $[R^{\cdot}_o] = 2 \times 10^{17}$ spins/gm (average of 6 readings see Table 6.2)

G-value total (i.e. $P^{\bullet} + M^{\bullet}$)

$$G_t = \frac{[R^{\bullet}]_o}{D_t} \times 100$$

$$\simeq 0.43$$

In order to determine the individual G-values, namely $G_{M^{\bullet}}$ and $G_{P^{\bullet}}$, a feel for their relative values must be at hand ;

If we use Dean's (D.1) conclusion i.e. $G_{M^{\bullet}} = G_{P^{\bullet}}$, therefore: $G_{M^{\bullet}} = G_{P^{\bullet}} \simeq 0.43$. If however, we use Chapiro's (C.4) hypothesis i.e. $G_{M^{\bullet}} = \frac{1}{2} G_{P^{\bullet}}$, therefore: total free radical concentration = monomer radicals + polymer radicals = total dose [(wt. % monomer x $G_{M^{\bullet}}$) + (wt. % polymer x $G_{P^{\bullet}}$)]

$$\frac{4.63 \times 10^{19}}{100} \times 0.02 \times G_{M^{\bullet}} + \frac{4.63 \times 10^{19}}{100} \times 0.98 \times 2\ G_{M^{\bullet}}$$

$$= 2 \times 10^{17} \text{ Free radicals/gm sample}$$

Thus:

$$G_{M^{\bullet}} = 0.218$$

$$G_{P^{\bullet}} = 0.436$$

Using the calculated G-values:

$$[R^{\bullet}]_o\ P = \frac{4.63 \times 10^{19}}{100} \times 0.98 \times 0.436$$

$$= 1.98 \times 10^{17} \text{ polymer radicals per gram sample.}$$

Similarly a value of: 0.02×10^{17} monomer radicals per gram sample is obtained. Thus, about 2×10^{17} polymer molecules out of 5×10^{18}/ gm, undergo the tranformation to free radicals. This is equal to 4% of the total number of polymer molecules. (this result is of importance in interpreting molecular weight data, which are to follow on P.139).

b) Calculation as applied to (c-1) (see App. I for analysis)

1 gm. of (c-1) contains:

$$5.8 \times 10^{21} \times \frac{7.05}{100} = 4.09 \times 10^{20} \text{ monomer molecules /gm sample}$$

$$\frac{N}{M_{P1}} \times 0.9295 = 4.4 \times 10^{18} \text{ polymer molecules /gm sample}$$

Where M_{P1} is the polymer molecular weight.

Total absorbed dose: D_t = 0.742 M rad

= 4.63×10^{19} e.v/gm. (see App.II)

The total free radical concentration measured experimentally at time zero after irradiation:

$$\left[R^{\cdot}_{o}\right] = 1.9 \times 10^{17} \text{ free radicals/gm}$$

(see Table 6.1)

Reapplying the same assumption, and following the same calculating procedure as for (c-2), the individual G-values were found to be:

$$G_{M^{\cdot}} = 0.213$$

$$G_{P^{\cdot}} = 0.426$$

iii) Discussion:

Chapiro et al. calculated $G_{M^{\cdot}}$ at dose rates ranging from 95.5 to 515 rads/sec., and obtained values varying from 0.30 to 0.46. Other $G_{M^{\cdot}}$

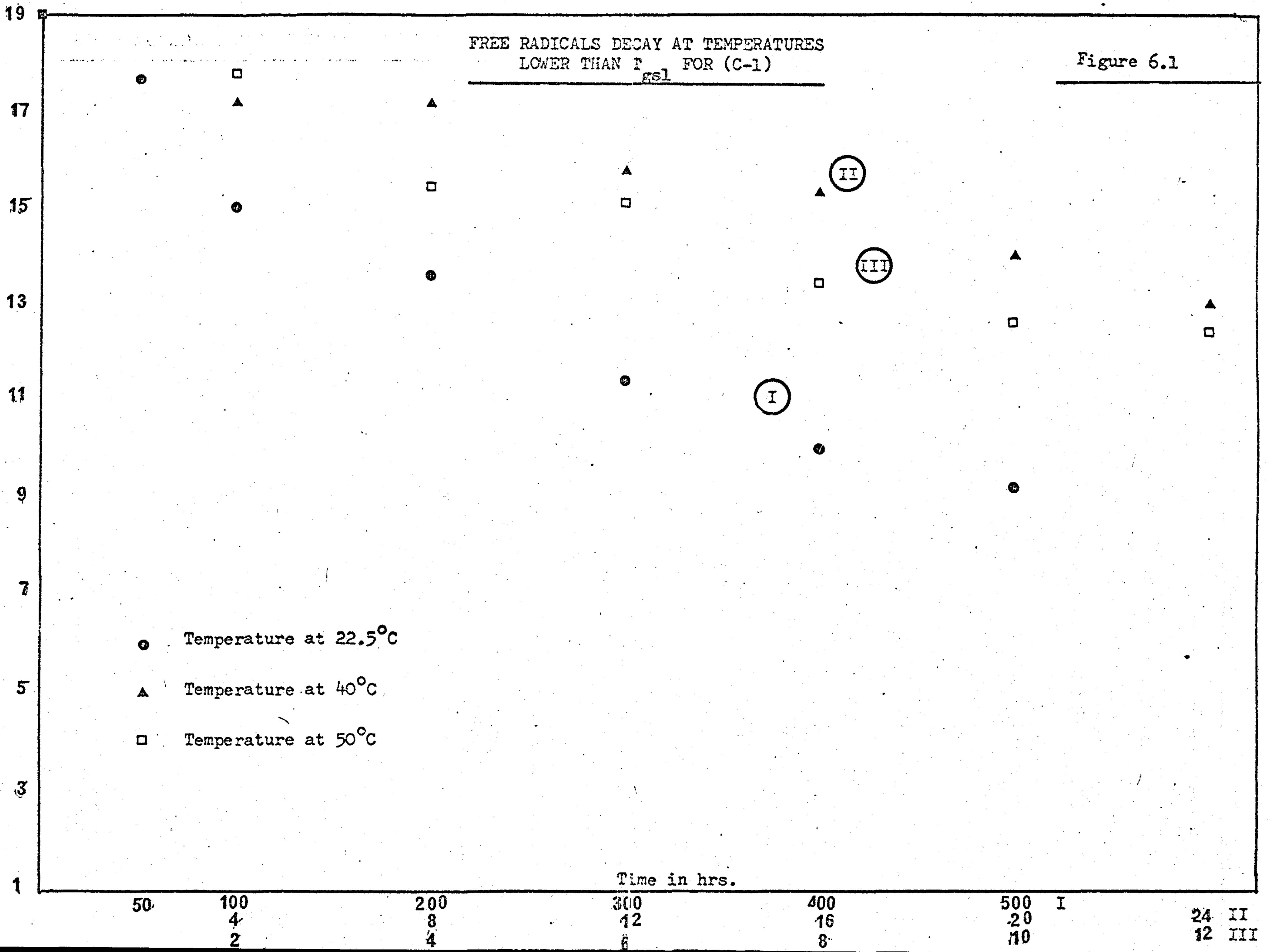
values are reported by Ref. (C.4) for dose rates 0.0059 to 78 rads/sec. He suggested an average $G_{M\cdot}$ value of 0.69 that exists up to a dose rate of 2-3 rads/sec. Further dose rate increase, causes $G_{M\cdot}$ to decrease sharply to values ranging from 0.22 - 0.46. Chapiro summarised all data in the form of a graph (Fig. E) relating the dose rate to $G_{M\cdot}$. He attributed the decrease in $G_{M\cdot}$ at high dose rates, found by numerous investigators, to a misuse of the simplified kinetic equation in a range of dose rates where it no longer applies, or to an inaccurate measurement of dose rate (e.g. data of Seitzer and Tobolsky).

According to the accuracy limitations in using the E.S.R. technique in determining the absolute free radicals concentration, (see Chapter IV and Ref. A.3, O.1, N.1), the average value of $G_{M\cdot} = 0.215$ and is within ± 50%. This value is based on the assumption that $G_{M\cdot} = 1/2\ G_{P\cdot}$. This implies that there is practically no chance for $G_{M\cdot}$ to be within the 0.69 range. If however, $G_{M\cdot}$ is equal to $G_{P\cdot}$ (D.1), (where the average computed $G_{P\cdot} = \frac{0.436 + 0.426}{2} \simeq 0.43$); it requires that the result is in error by (-50%) in order for $G_{P\cdot}$ to be in the neighbourhood of 0.69 anticipated by Chapiro (C.4). This possibility is considered remote. Consequently, the decrease in $G_{M\cdot}$ with dose rate increase, reported by many investigators, could be actually occuring and might as well have another explanation than Chapiero's. It is concluded that an excellent agreement exists for G-values calculated using (c-1), and those calculated using (c-2) samples. The average $G_{P\cdot}$ could be taken as = 0.43.

6.2.2 b & c Free radicals decay and the corresponding mechanism:

i) Related theoretical aspects:

Free radicals can only be terminated in pairs (B.7 and C.4). The

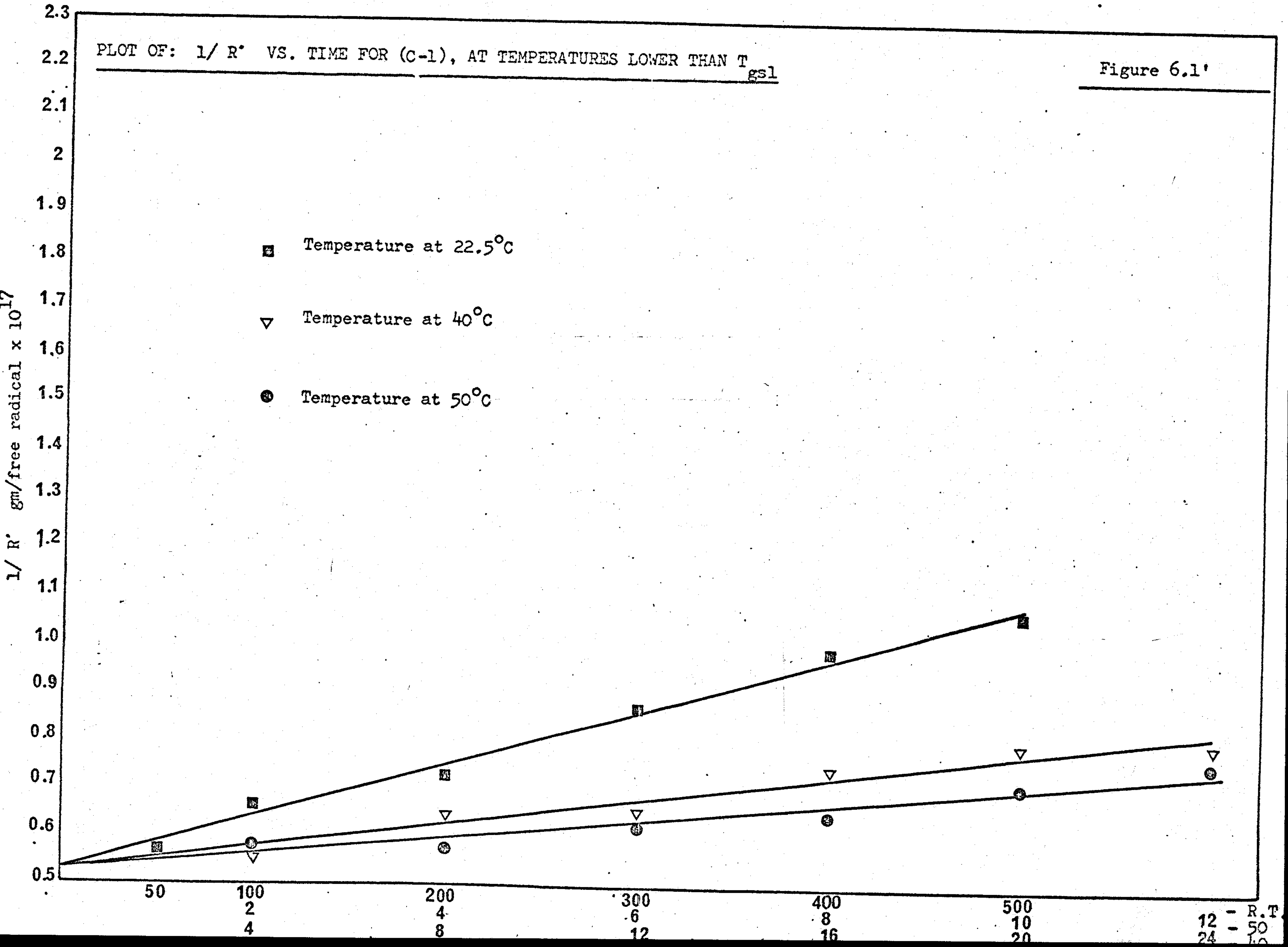


FREE RADICALS DECAY AT TEMPERATURES LOWER THAN T_{gsl} FOR (C-1)

Figure 6.1

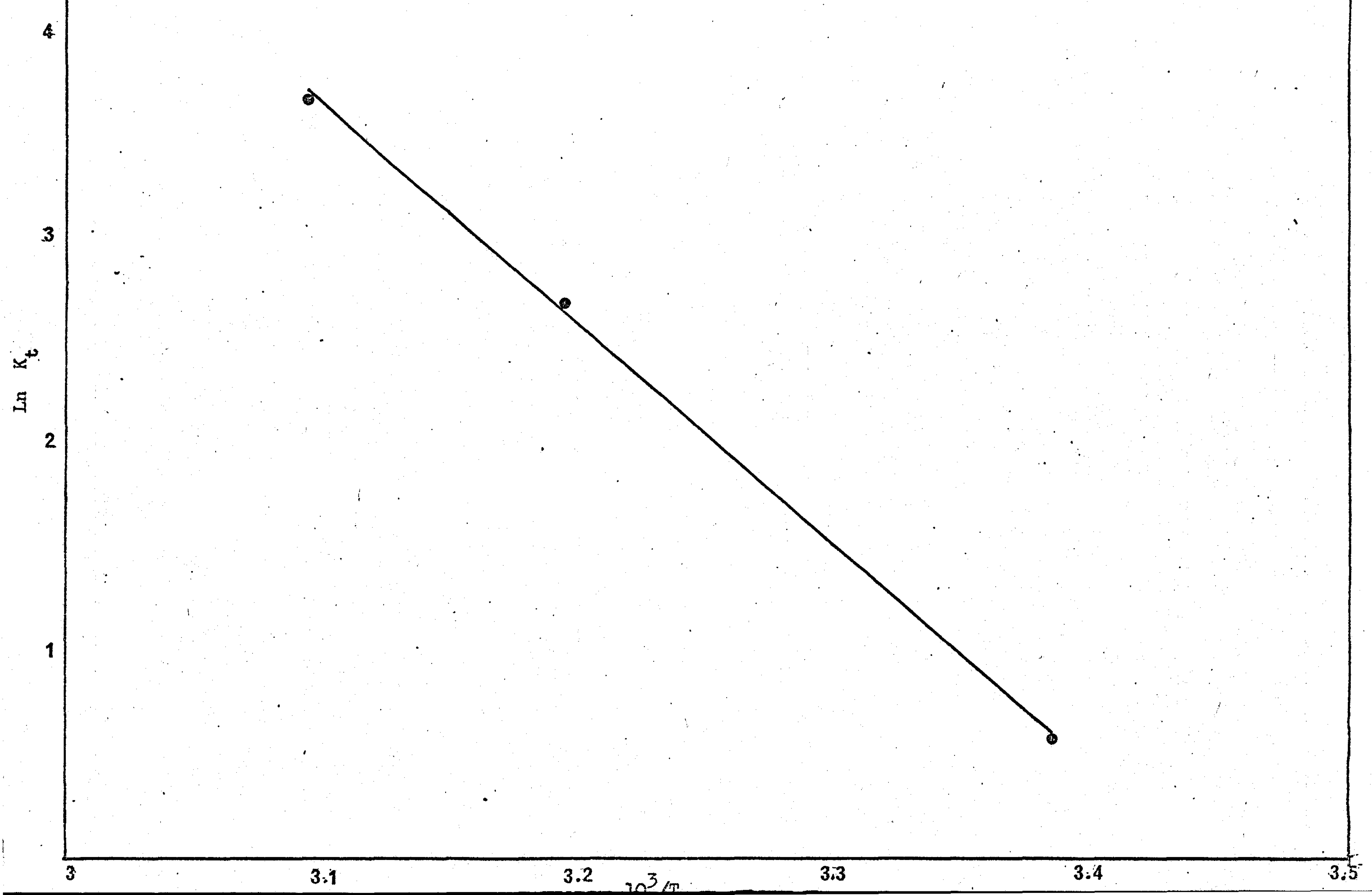
PLOT OF: 1/ R' VS. TIME FOR (C-1), AT TEMPERATURES LOWER THAN T_{gsl}

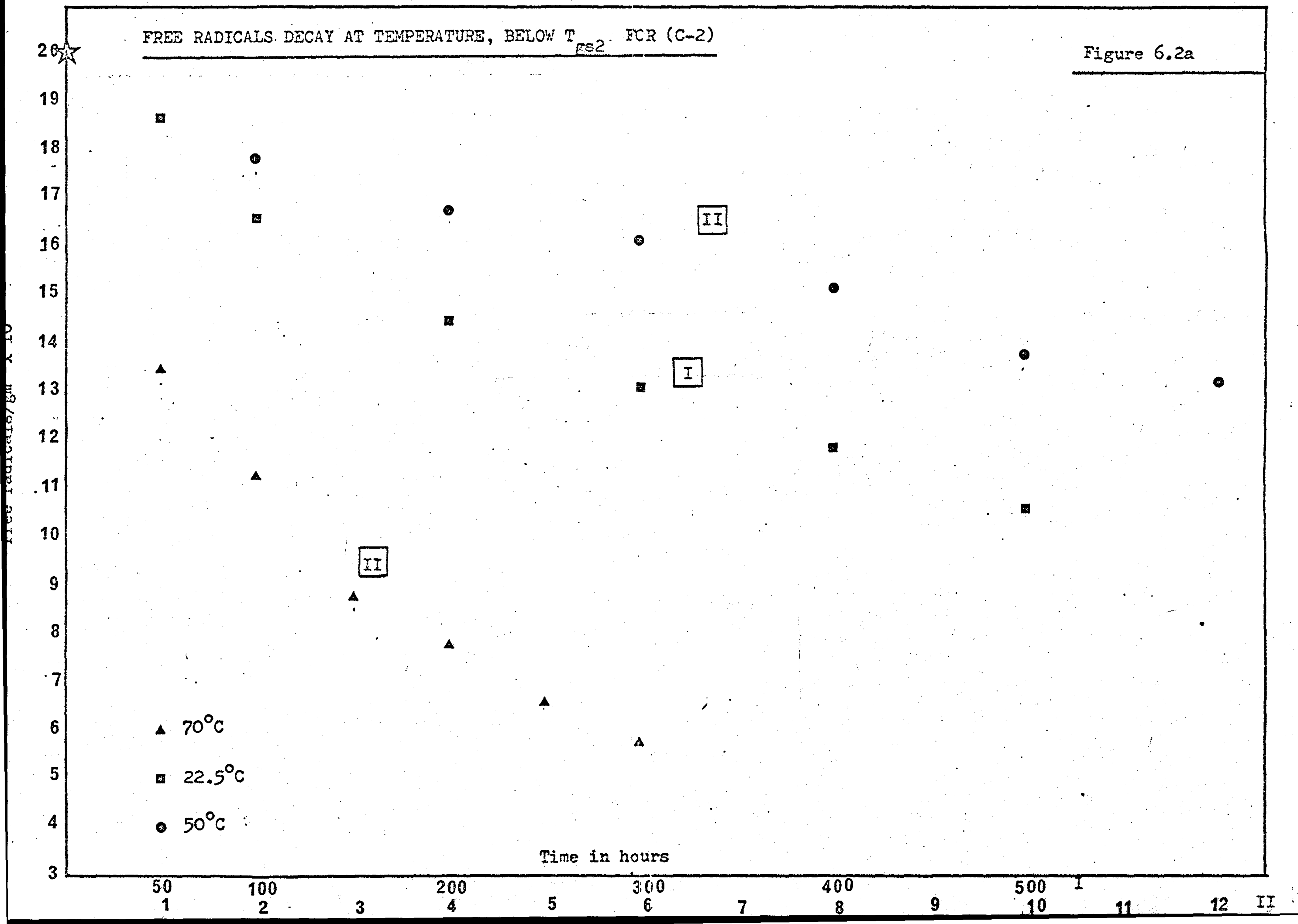
Figure 6.1'



FREE RADICAL'S DECAY AT TEMPERATURES LOWER THAN T_{gs2} FOR (C-2)

Figure 6.1"





FREE RADICALS DECAY AT TEMPERATURE, BELOW T_{gs2} FCR (C-2)

Figure 6.2a

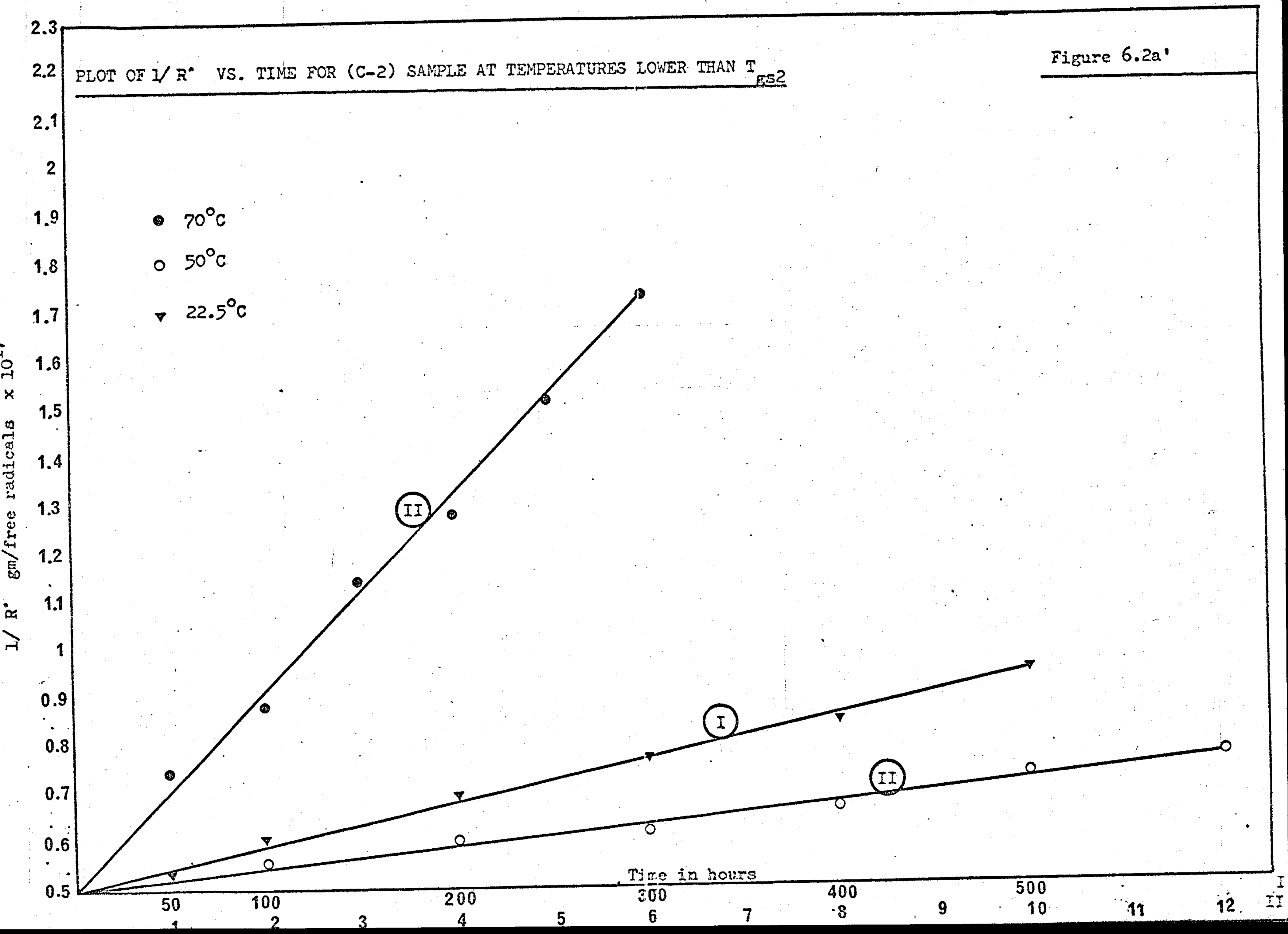
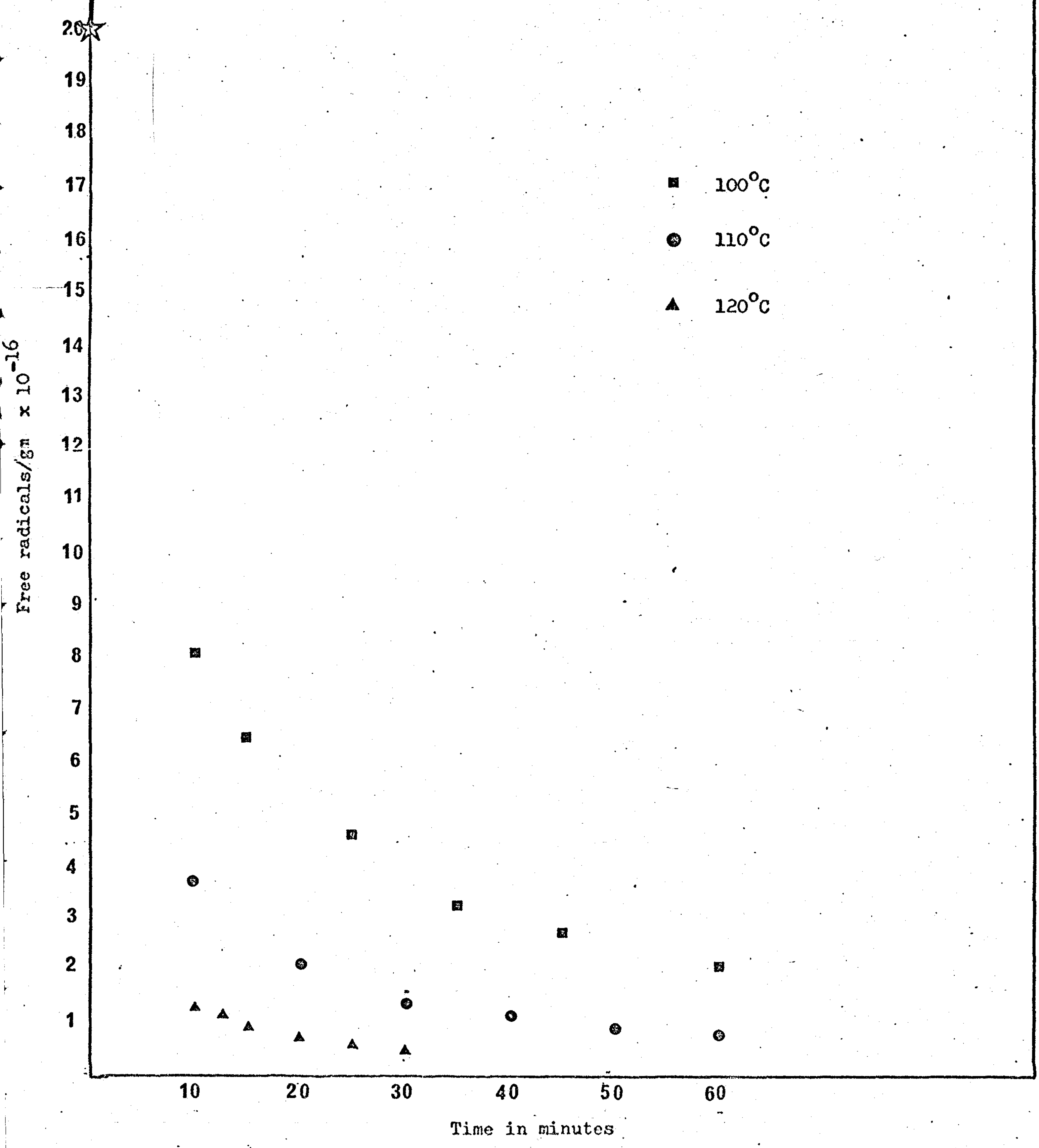


Figure 6.2a'

PLOT OF 1/ R˙ VS. TIME FOR (C-2) SAMPLE AT TEMPERATURES LOWER THAN T_{gs2}

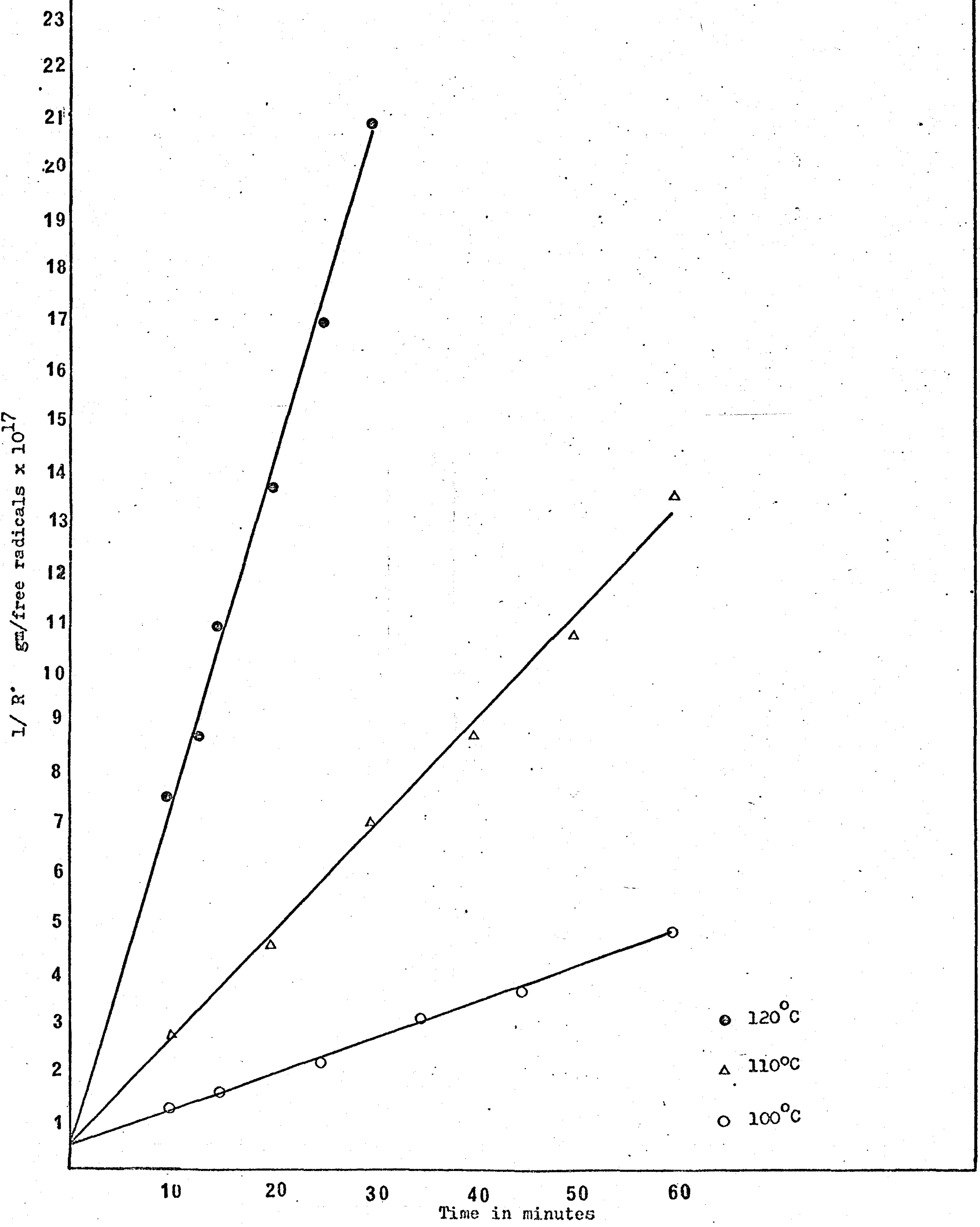
FREE RADICALS DECAY AT TEMPERATURES ABOVE T_{gs2} FOR (C-2)

Figure 6.2.b.



PLOT OF 1/ R' VS. TIME FOR (C-2) SAMPLES AT TEMPERATURES ABOVE T_{gs2}

Figure 6.2.b'



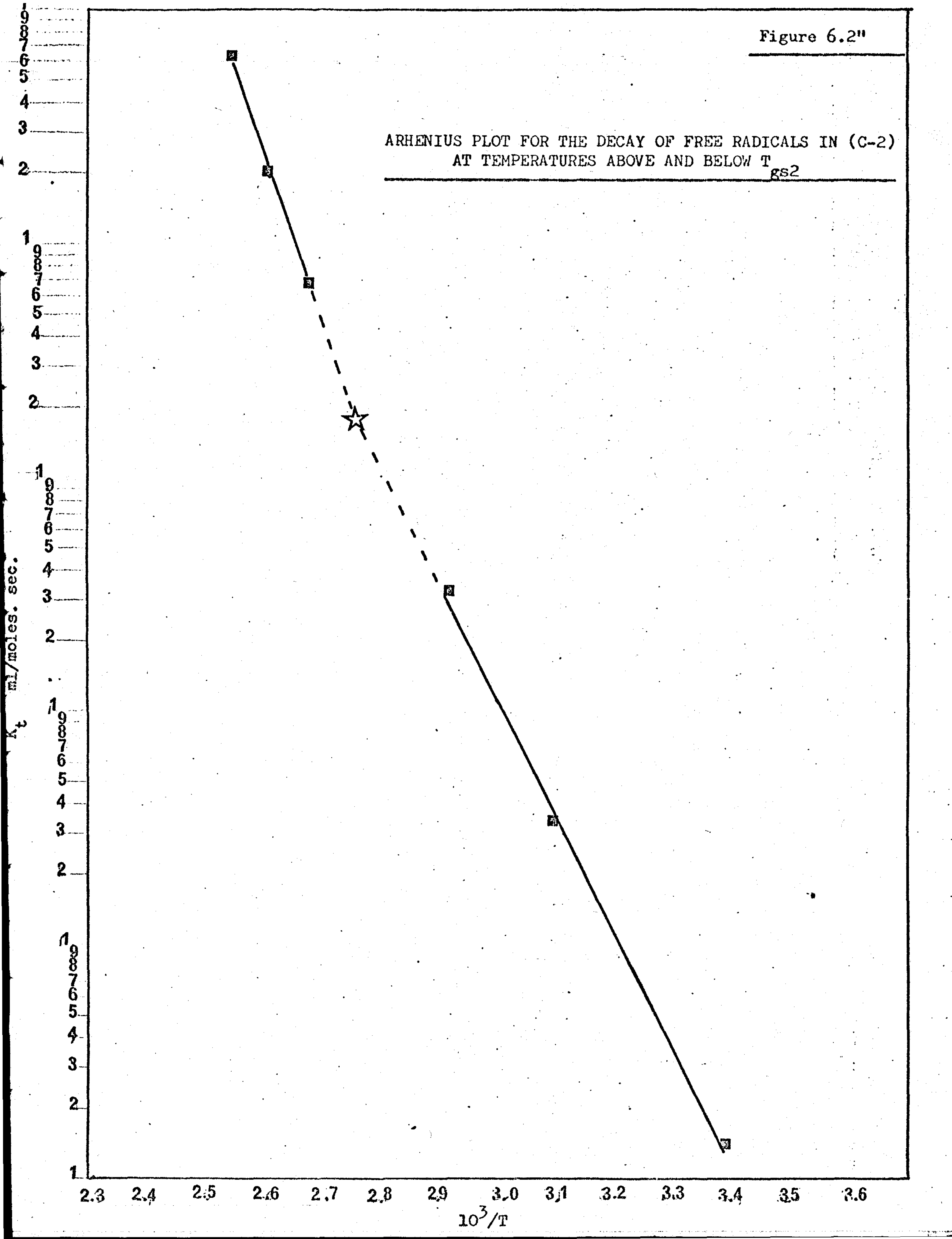
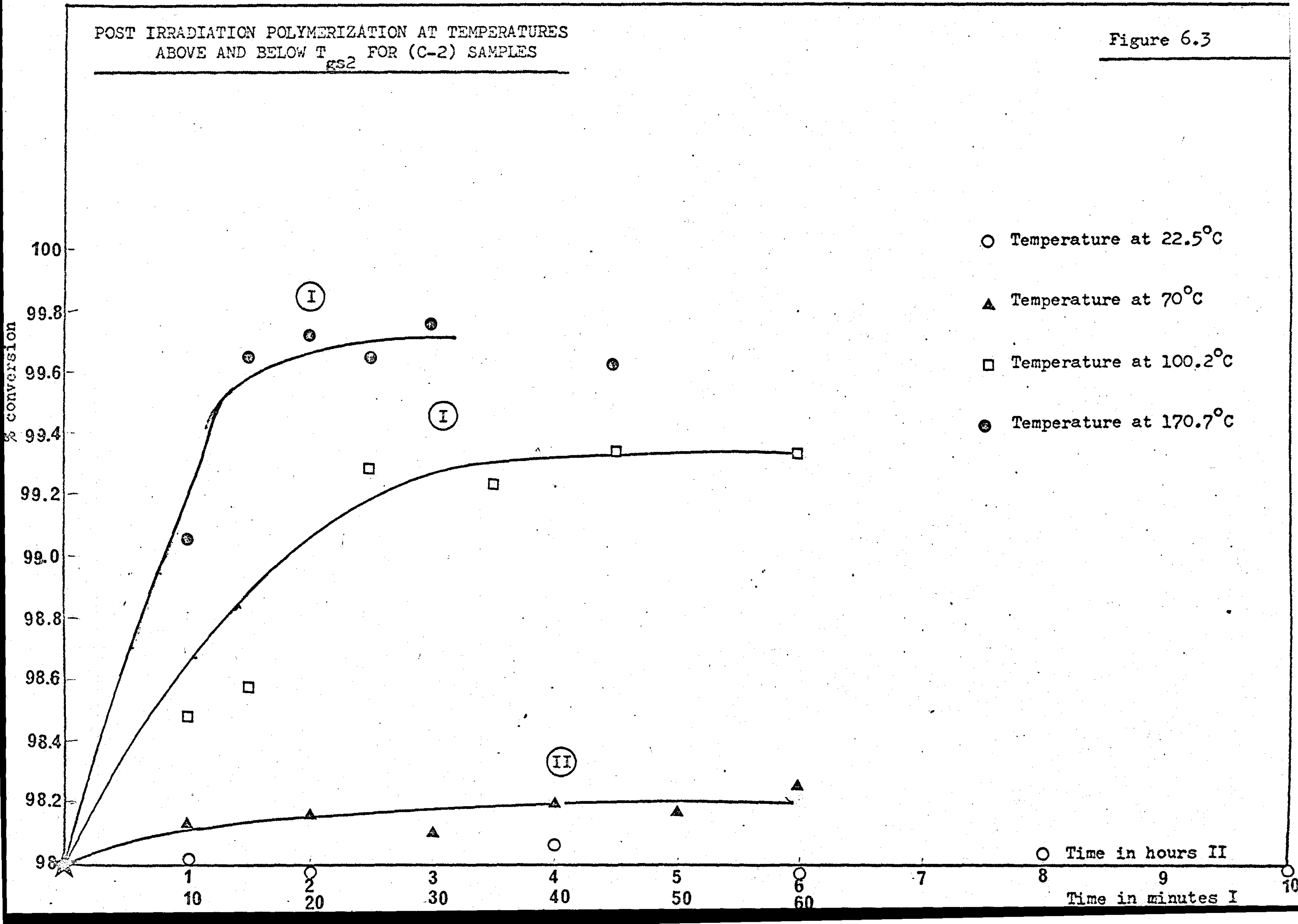


Figure 6.2"

ARHENIUS PLOT FOR THE DECAY OF FREE RADICALS IN (C-2) AT TEMPERATURES ABOVE AND BELOW T_{gs2}

Figure 6.3

POST IRRADIATION POLYMERIZATION AT TEMPERATURES ABOVE AND BELOW T_{gs2} FOR (C-2) SAMPLES



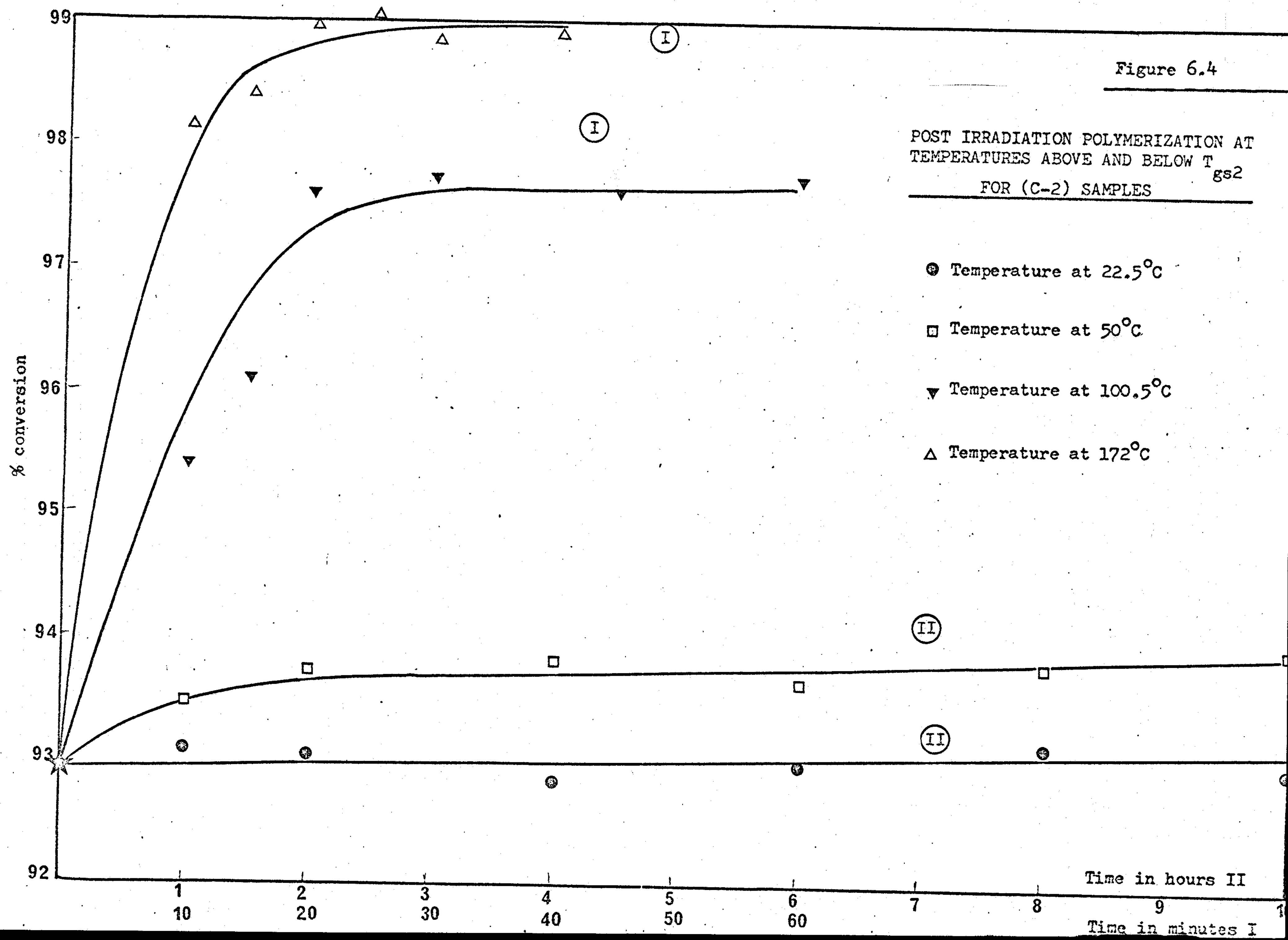
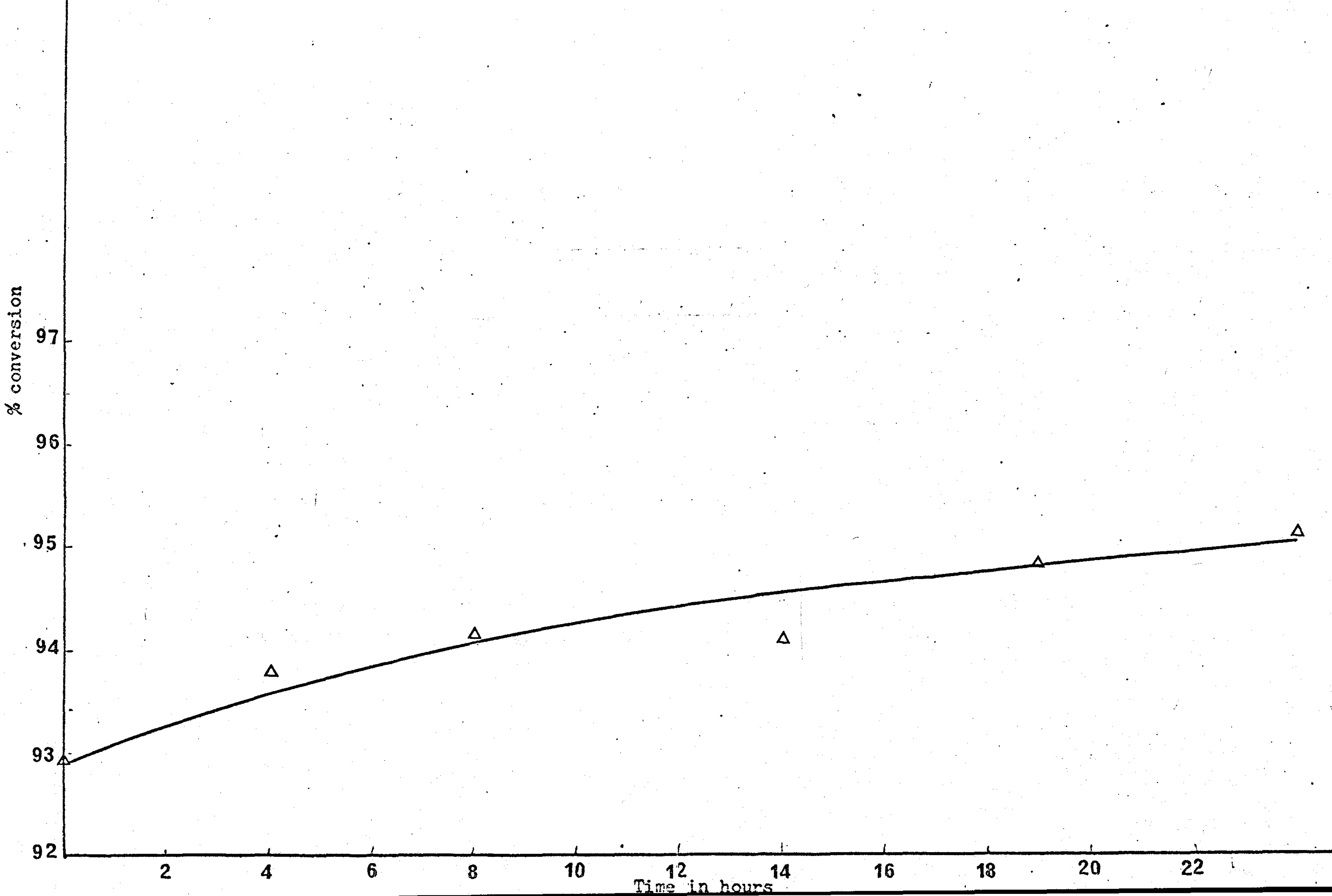


Figure 6.4

POST IRRADIATION POLYMERIZATION AT TEMPERATURES ABOVE AND BELOW T_{gs2} FOR (C-2) SAMPLES

THERMAL POLYMERIZATION OF (C-1) AT 100°C WITHOUT PRE-IRRADIATION

Figure 6.5



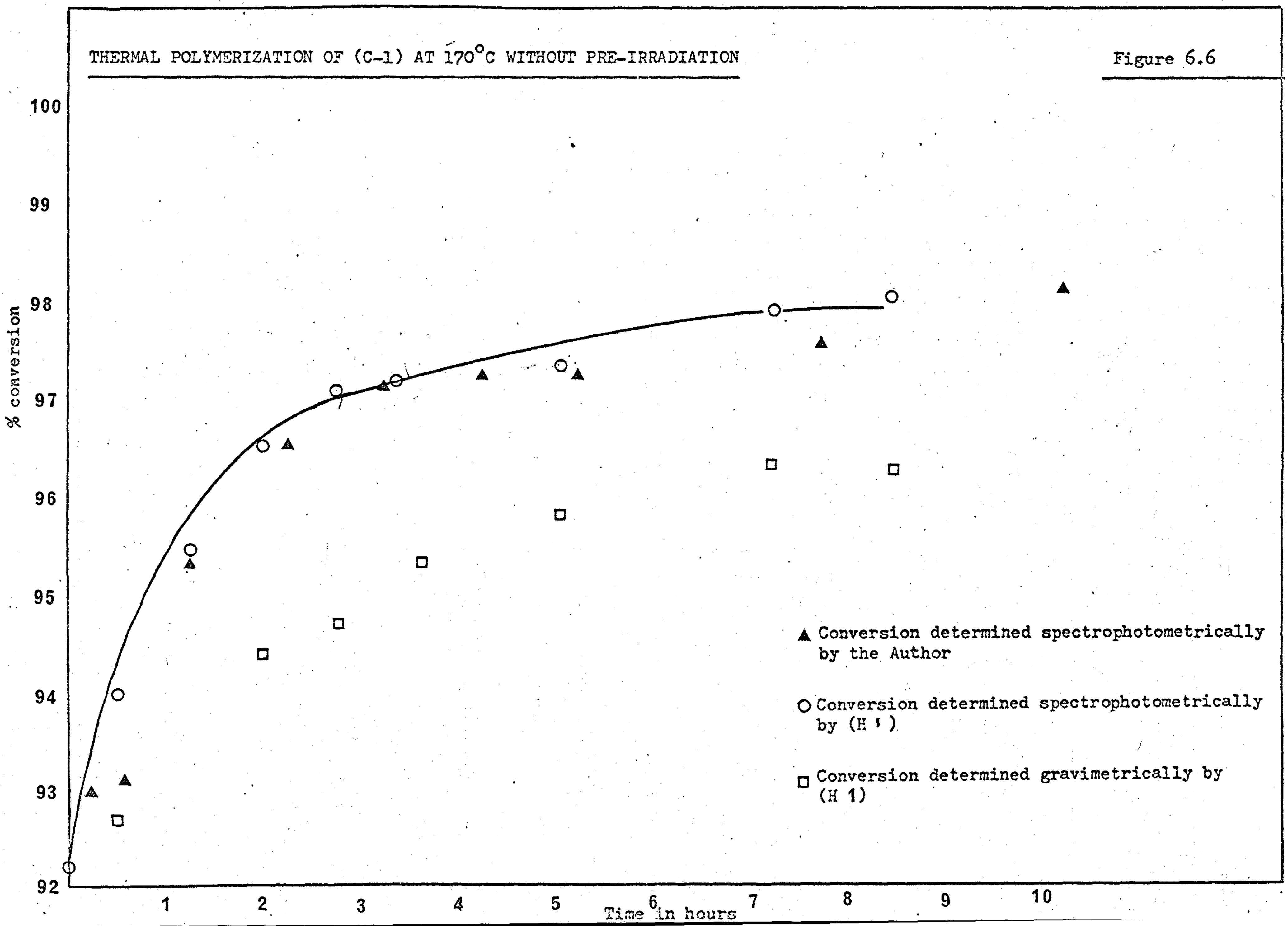

THERMAL POLYMERIZATION OF (C-1) AT 170°C WITHOUT PRE-IRRADIATION

Figure 6.6

kinetic scheme given in Chapter II, asserts this statement.

In the low conversion regions, chain termination is established to be of a second order nature. Fuji (F.7) reported a decline in the termination order starting from about 60% conversion. This suggests the occurrence of self termination i.e. polymer radicals become apparently terminated without mutual collision, due to the high viscosity developed, and to the shielding of free radicals by their polymer coils, making them inaccessible to each other.

The termination rate constant K_t was also found to decrease with conversion increase. (See Chapter II for details and literature review.) Several researchers have investigated the free radicals decay in pure polymers (100% conversion). Second order mechanisms, as well as first order ones, were reported (see Chapter II). The free radicals termination, was found to be of second order nature in the present investigation.

Rabinowitch's (R.1) equation for the rate constant Kt of a second order reaction is represented by:

$$K_t = \frac{A \exp(-E/RT)}{1 + (B \exp(-E/RT)/(D_1 + D_2))}$$

where E is the activation energy of the reaction. D_1 and D_2, are the diffusion coefficients of the two reactants.

When polymer chains can move freely, Rabinowitch's equation reduces to the classical Arrhenius form:

$$K_t = A \exp(-E/RT)$$

On the other hand, when D_1 and D_2 are much smaller than B exp (-E/RT), Rabinowitch's equation reduces to:

$K_t = A\ (D_1 + D_2)/B$

and $D = D_o \exp(-E_d/RT)$

where D_o = the diffusion coefficient at infinite dilution

E_d = the activation energy of diffusion

and if $D_1 = D_2$ (e.g. chain segments)

then $K_t = A.D_o \exp(-E_d/RT)/B$

$= A' \exp(-E_d/RT)$

where $A' = A.D_o/B$ = constant.

ii) <u>Assumptions</u>:

For the study of the termination mechanism of free radicals in (c-1) and (c-2), the assumption of K_t being constant throughout polymerization was put forward. This can be justified as follows:

a) All reported studies, attempting to relate K_t to the % conversion, were within the 20-70% conversion region, at which, the system is a viscous liquid undergoing a fast change in properties for every few percent increase in conversion. T_{gs} for such systems is far below 0^oC (see App.9), while temperatures at which investigations were carried out, are much higher than T_{gs}. Such is not the case with (c-1) and (c-2), for which, only a few percent monomer is in the system, causing it to be either in a glassy or a highly rubbery state, depending on the temperature.

b) Excluding the case where (c-1) samples are annealed at temperatures higher than T_{gs}; the change in conversion is so small, that K_t could safely be assumed a true constant over such a narrow range. As a result, free radicals decay studies were carried over (c-2) samples at temperatures above and below T_{gs2}, and over (c-1) samples at temperatures below T_{gs2} only.

iii) Mechanism of decay, and experimental results discussion:

A second order model, that could be represented by:

$$1/R^{\cdot} - 1/R^{\cdot}_{o} = K_t T$$

gave a reasonable fit at all investigated temperatures. Plotting $1/R^{\cdot}$ vs. T gives a straight line, its slope is the rate constant K_t, and the intercept is $1/R^{\cdot}_{o}$. A computer programme (App.VII) based on the least squares method (V_3), was used to obtain the best slope K_t, at each temperature, within 95% confidence limits. The linearity assumption was checked by computing the corelation coefficients (the latter were found to be very close to unity). The calculated rate constants can be found in table (6.3), and are given in 1/moles sec., (a sample calculation for the transformation spins/gm to moles/1 is given in App. IV). For free radicals decaying at room temperature and at 50°C, the values of K_t for (c-1) and (c-2) are close. The t-test for the difference between 2 slopes (see App. 8) have been performed, and the obtained value of t was greater than the tabulated one for the corresponding degrees of freedom. Therefore, it can be said that K_t for (c-1) and (c-2) at 50°C cannot be the same (at the 95% level). This might be attributed to the difference in the monomer content of the two systems.

6.2.2^{d}. Activation Energies of Decay:

A reaction rate constant can be represented by the Arrhenius equation (L. 4):

$$K = A \exp(-E/RT)$$

taking Logarithms:

$$\ln K = \ln A - E/RT$$

Similarly, Rabinowitch's equation reduces to:

$$\ln K = \ln B - E_d/RT$$

for diffusion controlled reaction. Thus plotting:

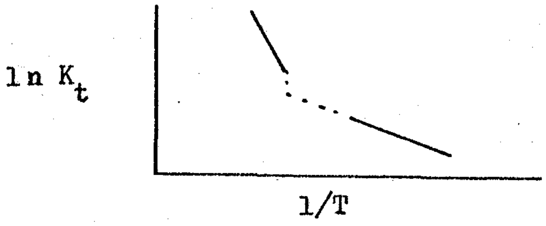
$$\ln K \text{ vs. } 1/T$$

gives a straight line whose slope = $-E/R$, where E is the activation energy, and R is the gas constant.

6.2.2d.1. Activation Energy for (c-2):

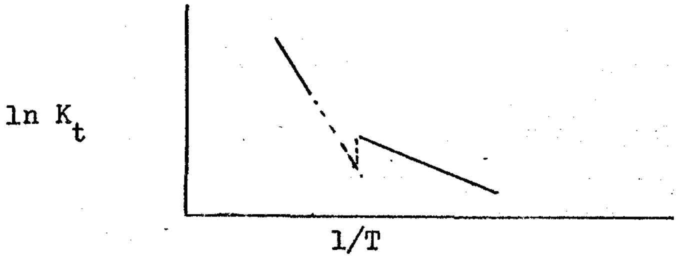
Plotting ln K vs. 1/T, six points were obtained, which were found to be better represented by two straight lines (Fig. 6.2"). The least squares method (V.3) was used to find the best fit, (see App. VII). The correlation coefficients were computed and were found to be extremely close to unity. At temperatures lower than T_{gs2}, the apparent activation energy of decay for (c-2) was found to be 22.9 K cal/mole (see Table 6.3, and App. VII). On the other hand, a value of 32 K cal/mole was obtained for the decay at temperatures higher than T_{gs2}, A t-test was performed to compare the two slopes (see App.8), and the obtained t value was found to be higher than the tabulated one at the appropriate degrees of freedom (at the 95% level), indicating that it cannot be said that the two lines have the same slope (at this level). The slopes of the two lines were subjected to a severe and bias test. A line was drawn between the lower confidence limit of K (at 22.5°C) and the higher confidence limit of K_t (at 70°C), and the obtained line was compared to a line drawn between the higher confidence limit of K_t (at 100.2°C) and the lower confidence limit of K_t (120.5°C). The result showed that the activation energy below T_{gs2} is less than activation energy above it, even by using such a severe test. During the course of polymerization, the theoretically estimated T_{gs2} increases from about 87°C to a maximum of about 96°C at the highest temperature tested (see App. VII). By extrapolating the two obtained lines, the intersection was found to be at about 91°C. This value is within the range (87-96°C) theoretically estimated. The agreement between the theoretically estimated T_{gs2} and the experimentally obtained one, is remarkable. This indicates the validity of the assumptions made throughout the process. However, other possibilities still exist.

1) Instead of extrapolating the two lines, extrapolate only the lower one:



This suggests a sudden increase in the frequency factor, at the glass transition temperature. This behaviour is not unlikely since suddenly the chains have more freedom to move as the temperature reaches T_{gs}. This however, shifts the discontinuity in the Arrhenius plot to a little over the theoretically estimated T_{gs}, but this difference could be accepted as an experimental error.

2) Extrapolation of the steeper line only:



This is the case where a sudden decrease in the frequency factor applies. A tentative explanation could be: as a larger entity might be moving, the vibration frequency might be less. If this is the case, then the difference between the experimental and theoretical $\dot{T}_{gs}$ is too high to be accepted.

All sorts of deflections and discontinuities in the Arrhenius plot occuring at the glass transition temperatures and melting points, could be found in the literature. (Chapter II gives several examples.)

An example of close similarity to our case is the work by Ref. (O.1), who studied the decay of free radicals in PMMA. It almost perfectly fitted a second order mechanism. The rate constants in the glassy region were determined and were found to be in the same order of magnitude as those obtained for polystyrene, in this investigation. Ref. (O.1) reported an activation energy for decay of 28K cal/mole at T less than T_{gp}.

A change in the activation energy, with a phase change, is a common phenomenon, but the observed increase in the transformation from a glassy state to a rubbery one (22.9 to 32) is not simple to imagine. One would rather expect a diminuation in the mediums resistance (i.e. a smaller barrier for the decay reaction) associated with such a change.

However, Deutsch et al. (D.2) reported for the α transition of PMMA a value of 80 K cal/mole using mechanical measurements, and for the β transition values of 18 and 20 K cal/mole obtained by audio frequency vibrations method and dielectric properties measurements, respectively.

In nuclear magnetic resonance study of PMMA (P.4), Powles, estimated the activation energies for the α and β transitions to be 27 ± 10 K cal/mole, and 18 ± 4 K cal/mole, respectively. The greater activation energy in the α region over that in the β one, implies a <u>larger moving</u>

entity. This has been attributed to the association of the β region with the mobility of the carboxymethoxy groups, while in the α one, we get the motions of chain segments in addition.

This explanation might well be applied to clarify the results obtained in the present investigation. The activation energy obtained for the reaction in the glassy state might be attributed to the vibrating movement of the chain end carrying the free radical, and the moving entity would be the free radical unit plus a few monomer units that might be attached to it. The transformation to the rubbery state does not allow polymer chains to slip over one another, i.e. the chain centre of gravity remains fixed. However, chain segments become liberalised, and can move freely (which is not the case in the glassy state), The increase in activation energy associated with this transformation. can be therefore attributed to the motion of a larger entity.

6.2.2d.2 Activation Energy of (c-1): (effect of % monomer)

(Figure 6.1") and Table 6.3) show that for free radicals' decaying in (c-1) at T less than T_{gsl}, an activation energy of 21.4 was obtained using the same method of analysis as in (c-2). This value is close to the value obtained for (c-2) in the same temperature range. (App. VIII) demonstrates the statistical method employed in comparing the two slopes (t-test). According to the value obtained for (t), the lines could not be treated as having two statistically different slopes.

Thus it can be concluded that a difference in monomer concentration does not necessarily cause a change in the activation energy as long as the system is in the glassy state. However, this statement cannot be asserted until further studies are performed, using samples with larger differences in monomer concentration, to enable accurate determination of the effect of % monomer on the activation energy of free radicals decay.

6.2.2e Post Irradiation Polymerization:

i) Related theoretical aspects:

The kinetics of conventional polymerization can be represented by either the simplified scheme, or the detailed one, given on (Chapter II). This kinetic applies only to low conversion polymerization. Deviations start to occur sometimes as low as at 10% conversion. The middle region of conversion, characterized by a sudden acceleration in the rate of polymerization (Tromsdorff's effect), has been investigated. A qualitative treatment is established. Mechanisms were suggested, some of which represent the kinetics fairly good, up to 40% conversion. This region extends to about 80% conversion, and sometimes to 90% conversion, after which a sudden and sharp drop in the rate is noticed, followed by an almost complete cessation of polymerization before the completion of the reaction, under the normal conditions.

Roche and Price (R.3) produced the conversion vs. time plots for the thermal bulk polymerization of styrene at various temperatures, up till about 90% conversion. It was found that it takes about 60 days to reach 99.5% at 125°C (B.17). Rates as much as 60% higher than Roche and Price's were reported by Schulzet et al. (S.5) at temperatures 79.5 - 131.5°C. Mark and Raff came up with intermediate values, do did Hui and Hamielec (see Figures A and B) (H.1, H.10). So far, very little is known about the last 10% conversion region.

ii) Discussion of results:

Conversion vs. time plots for (c-1) at 170°C and 100°C without pre-irradiation are given in Figures 6.5 and 6.6). These are used for comparison with the (c-1) samples, which have been irradiated, before annealing at 172°C and 100.5°C. (Figure 6.4).

(Note: the small difference in the reaction temperatures was caused by the heat of the fast reaction, and it is obvious that the latter is not the cause for the dramatic rate difference in both cases.)

Post-irradiation polymerization studies, can be found in the literature. Investigation was chiefly concerned with irradiating a solid monomer(i.e. 0% conversion) at low temperatures, and post-irradiating at higher ones. Bowden (B.18) applied such treatment to octadecyl methacrylate (other examples can be found in Chapter II). The post-irradiation polymerization is characterized by a very high initial rate, followed by a sharp, sudden decrease.

Bowden (B.18) took advantage of this shape in treating the linear part of each conversion vs. time plot as a zero order reaction, which he called the apparent initial overall rate, Rio, and determined it as a function of time. Arrhenius relation was used to find the activation energy for Rio and was found to be 20 K cal/mole.

The post-irradiation polymerization curves for (c-1) and (c-2) were similar in shape to those reported in the literature for experiments starting at 0% polymer. Although it was possible for Bowden (B.18) to treat his data in this peculiar way, which served only in providing a feel for the effect of temperature on the apparent initial overall rate, but did not specify any mechanism for the individual reaction steps, it was felt that attempting to treat the data obtained for (c-1) and (c-2) in a similar manner, is not justified. This can be explained as follows:

1) All rate constants at this conversion region are probably a function of % conversion. This is probably not the case with Bowden's investigation since he was dealing with a low conversion region.
2) Assuming that rate constants and activation energies, are true constants over the slight observed change in conversion, proved to be successfully used in the analysis of free radicals' decay data. Several factors prevented taking this approach as applied to the whole polymerization reaction:
   a) The observed change of conversion is so small, that a deduction of values for reaction rates, might be in great error. This is not the case in free radicals' decay, for which the amount of change is substancial and therefore, any experimental error will be relatively small.
   b) (4.5) experimental points fell in the levelling off region, leaving just (2-3) data points to help determine the initial rate. This is considered statistically poor. Accordingly, all experiments should be repeated on a smaller time scale in order to overcome this difficulty. This, as has been proved in Chapter IV, is very difficult to achieve experimentally at high temperatures (as applied to this experimental setting).

Kaetsu (K,1) stated that if in-source polymerization occurs, post-irradiation polymeriation does not take place. On the other hand, if irradiation causes no in-source polymerization at the specific temperature, post-irradiation polymerization may occur at higher ones. The latter part of the statement proved to be correct, but the first half seems to need some refinement.

(Figure D) indicates that by irradiation at 50°C polymerization occurs to completion. (Figure 5.10) shows that stopping radiation (at 50°C), after the system passed from the rubbery to the glassy state, allows some free radicals to accumulate, due to the relatively slow decay rates at T less than T_{gs}, causing fast initial post-irradiation polymerization rate.

Horie et al. (H.7), studied the thermal polymerization of methylmethacrylate and styrene. Their data indicates the cessation of polymerization when the system reaches T_{gs}, i.e. a limiting conversion will always be shown, if the system is polymerized at temperatures less than T_{gp}. The limiting conversion is the composition corresponding to a T_{gs} equal to the polymerization temperature. On the other hand, by using irradiation, Hodgins (H.3), for example, proved that this is not the case, since he brought reaction to completion at 50°C, 70°C, and 85°C, while $T_{gp} = 100°C$. Moreover, a limiting conversion is shown in the present investigation, even when temperatures exceed T_{gp}. Therefore, the limiting conversion needs more investigation to be adequately explained.

6.2.2f. Effect on Molecular Weight:

i) Theoretical aspects:

Different types of molecular weights characterize the polymer. They have been briefly discussed in (Chapter IV).

Collegative property measurement is used to determine M_n, and the most successful method uses osmometry, according to the relation (C.12):

$$\lim_{c \to o} \frac{\pi}{c} = \frac{RT}{M_n}$$

Where:

π = osmotic pressure.

c = concentration.

R = gas constant.

T = temperature.

A sample calculation is given in (App. 10) accompanied by the theoretical and experimental aspects of this technique.

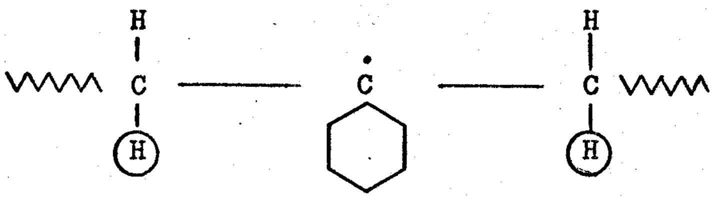
ii) Discussion of results:

Accurate measurement of changes in the M_n can lead to indicate whether termination is occuring by combination or by disproportionation. It might also show if substancial transfer to the monomer is taking place. However, initial M_n data obtained during the post-irradiation annealing of (c-1) and (c-2) (see Table 6.4) indicated the fruitlessness of further investigation. This is due to the low $[R^\bullet]$ free radical/$[P]$ dead polymer ratio (about 4%), and to the accuracy limits of the measurement method (about 5%). It was therefore concluded that the present experimental conditions cannot yield information to indicate the nature of the termination reaction, nor the role of the transfer action.

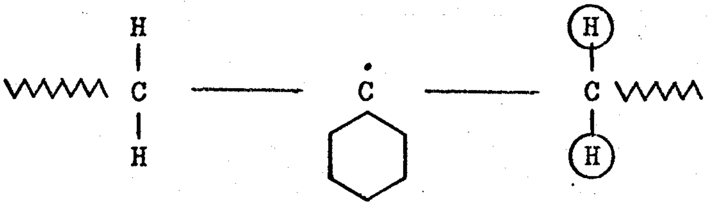
6.2.2g. Structure of the obtained free radical:

Electron Spin Resonance can help in the identification of free radicals, however, it is a very tedious and sophisticated technique. Florin et al. (F.1) studied the gamma irradiated polystyrene and deuterated polystyrenes. Small changes in shapes of the E.S.R. signal were observed, depending on the irradiation temperature and the temperature at which measurements were carried out (see Chapter II). The signal obtained in the present investigation resembles that obtained by Florin. A resume of his interpretation follows:

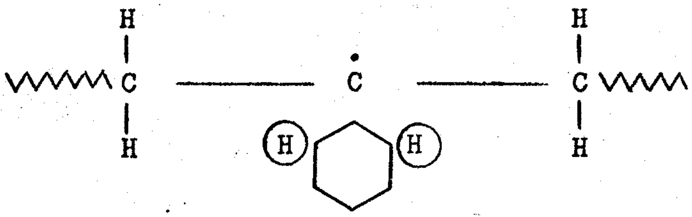
The obtained similarity of all deuterated polystyrene spectra indicates that the radical cannot have strong hf. interaction with any main chain hydrogens, such as:



or



Nevertheless, strong chemical arguments favour the radical mentioned. Therefore, it is proposed that the radical has the shown structure but the principal hf. interaction is with the two ring hydrogens in the ortho positions:



Florin also gave arguments for the reason of excluding positions other than the ortho ones (see Chapter II).

CHAPTER VII

Summary and Conclusion

7.1 Experiments starting with pure % monomer:

This approach faced some experimental difficulties, nevertheless, some conclusions were deduced:

a) No post-irradiation effect is observed if polymerization by radiation was stopped at compositions corresponding to T_{gs} below irradiation temperature.

b) The anticipated molecular weight differences in systems polymerized by using varied dose rates caused only little effect on the post-irradiation polymerization rates.

c) Polymerization can be taking place in-source followed by a positive post-irradiation effect (Figure 5.10). This phenomenon occurred only when irradiation was carried until the system passed to the glassy state.

7.2 Experiments on (c-1) and (c-2) samples:

The relation between T_{gs} and the system's composition helped in choosing an irradiation temperature (room temperature), and post-irradiation temperatures (above and below T_{gs}).

In order to trap radicals (in high concentrations) in a styrene-polystyrene system when irradiation is at room temperature the system must be 82.5% (by volume) conversion or higher (see App. IX) (T_{gs} at 82.5% = room temperature).

- G_p. value was obtained $\simeq 0.43$ and by putting:

a) $G_{M^\cdot} \simeq 1/2\ G_{P^\cdot}$, (C.4), therefore $G_{M^\cdot}$ is about 0.22

b) $G_{M^\cdot} \simeq G_{P^\cdot}$, (D.1), therefore $G_{M^\cdot}$ is about 0.43

- These values are within ± 50%. This agrees with other published data in this region of dose rates and contradicts Chapiro's argument about $G_{M^\cdot}$ being actually a constant (0.69), throughout all dose rate ranges.
- Free radicals were detected by irradiating (c-1) and (c-2) at room temperature. The trapping efficiency seems to be the same for both systems inspite of the difference in % monomer. This might be due to the fact that:

  1) Both are in the glassy state.

  2) Both correspond to a T_{gs} much higher than room temperature.
- Free radicals were found to obey a second order decay, to a fair degree. Rate constants and activation energies for decay have been calculated.
- A discontinuity was detected in the Arrhenius plot showing an increase in the apparent activation energy of the termination reactions in the rubbery state over that in the glassy state. The latter might be attributed to a larger moving entity, namely: a chain segment as opposed to the radical end group.

Chain transfer might have a role in the termination mechanism, but this cannot be asserted due to the accuracy limitations of molecular weight determination methods. The same applies for the nature of the termination reaction whether combination or disproportionation. These can only be experimentally measured if $[R^\cdot]_0$ was about five folds greater, so that $P^\cdot/P$ will be substantial.

- Through statistical analysis it was shown that at the 95% level, the rates of decay are somewhat faster for systems with higher % monomer. For the activation energy, on the other hand, it cannot be said (95% confidence level) that it is different for (c-1) and (c-2). The obtained values, however, indicate that the assumption that K_t is practically constant over small changes in conversion, is justified, since only a slight difference was obtained between values of K_t at a relatively large difference in % conversion. The same is also true for activation energies.
- Post-irradiation polymerization was found to be very little at temperatures below T_{gs} (although it seems to be zero at room temperature but it is likely that some polymerization might occur if it were analysed over a period of about a month. On the other hand, at temperatures above T_{gs}, very high initial rates were observed (behaving as zero order reaction), followed by a sudden and sharp decrease to an almost cessation of the reaction. In this respect it behaves in quite an identical manner to experiments carried on irradiated monomer reported in the literature.
- No attempt was made to determine apparent initial overall rates due to the fact that they are probably associated with an intolerable % error (due to measurement limitations) especially in cases of slight conversion changes (where the assumption that rate constants are practically constants, can be applied).
- The limiting conversion increases by temperature increase, but seems not to be related to T_{gs}.
- Molecular weight measurements were found to be of no great value, since

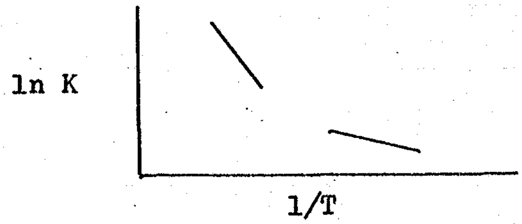
the measurement's accuracy limitations, practically engulfs foreseen changes. This can be attributed to the low $P':P$ ratio.

- The E.S.R. signal was found to resemble that of Florin (F.1), a resume for his interpretation of the structure is given.

Suggestions for Future Investigations

1) The determination of K_t can proceed to lower conversion regions (e.g. down to 85%). Polymerization must always be carried over a small range to enable the use of the assumption that K_t is a true constant over such a narrow range. This method can provide different values of K_t over a wide range (e.g. 85% to 100%). The change of K_t with conversion at such high regions can therefore be investigated.

2) More experimental work can be carried out to fill the gap in the Arrhenius plot. Also, similar to K_t, the effect of % monomer, on the activation energy, needs more experimental datta to establish it.



3) Irradiation might be carried out for much longer periods of time with the aim of creating a higher concentration of free radicals (perhaps fivefold). Thus, the ratio $R^{\bullet}/P$ would be higher, and M_n measurement might clarify the nature of the termination reaction (whether combination or disproportionation).

APPENDIX I

Samples & Chemical Analysis:

1) Sample (c-1):

Monsanto Analysis (22, 4, 1969) = 7.6% residual monomer

Authors Analysis (August 1969) = 7.05% residual monomer

M_n = 126,600

M_w = 339,000

M_w/M_n = 2.68

2) Sample (c-2):

Monsanto Analysis = 2.1% Monomer

Authors = 2.0% Monomer

M_n = 120,000

M_w = 355,000

M_w/M_n = 2.96

3) Chemicals:

Methyl alcohol, Chloroform, Toluene, dioxane are all of reagent grade quality.

4) Styrene monomer:

Uninhibited pure styrene. Chemical composition is given in Ref. (D.1).

APPENDIX II

<u>Conversion Factors</u>:

1 rad = 100 ergs/gm

= 6.24 x 10^{13} e.v/gm

= 2.78 x 15^{9} watt. he/gm

1 M rad = 10^{6} rad = 10 joules gm^{-1}

Ref. (S.17 and C.4).

APPENDIX III

Estimation of the density of the system:

Polystyrene density = 1.06 (B.17)

Styrene density = 0.9019 (B.17)

Assuming the additivity of volumes:

1. Sample (c-2):

The volume of 1 gm sample = $0.98/1.06 + 0.02/0.9019 = 0.947$ ml.

Thus, the density = $1/0.947 = 1.0566$ gm/ml.

2. Sample (c-1):

Similarly a value of: 1.050 gm/ml. was obtained for the density of (c-1).

APPENDIX IV

Concentration of Free Radicals at time zero $[R^{\bullet}]_{o}$

1. Sample (c-2):

Free radical concentration = 2×10^{17} spins/gm

1 gm mole = 6.023×10^{23}

Free radical concentration = $\dfrac{2 \times 10^{17}}{6.023 \times 10^{23}} = 3.32 \times 10^{-7}$ moles/gm.

Density of the mixture = 1.0566 gm/cm^3 (App. III).

Concentration of free radicals = $3.32 \times 10^{-7} \times 1.0566$

= 3.51×10^{-7} moles/ml.

= 3.51×10^{-4} moles/l.

2. Sample (c-1):

$[R^{\bullet}]_{o}$ = 1.9×10^{17} spins/gm.

= $\dfrac{1.9 \times 10^{17}}{6.023 \times 10^{23}}$

= 3.155×10^{-7} moles/gm.

Density = 1.05 gm/ml. (App. III).

Free radical concentration = $3.155 \times 10^{-7} \times 1.05$

= 3.31×10^{-7} moles/ml

= 3.31×10^{-4} moles/ml

APPENDIX V

Estimating Styrene's glass transition temperature (T_{gm}):

Ueberreiter and Kanig (U.1) related the glass transition temperature to the molecular weight as follows:

$$1/T_g \quad = \quad (1/373) + (0.517/M)$$

For polystyrene fractions of $M \geqslant 200$.

Assuming extrapolation could be applied, and putting M=104

Therefore:

$$T_g \simeq 131^{\circ}K \quad = \quad -142^{\circ}C$$

The value of the constant was put as (0.864) by Fox and Loshaek (F.5), but was found to give an illogically low value for T_{gm}. This was also based on a similar case, where Chapiro (C.7), experimentally measured T_{gm} for methyl methacrylate and found it to be $-106^{\circ}C$, while it was thought to be around $-130^{\circ}C$.

APPENDIX VI

Statistical Analysis of results:

a) As applied to the termination rate constants (K_t):

A computer programme using the least squares (V_3) method was used. (See App. VII.) The following values have been calculated:

- The best fit, leading to determine the slope K_t.
- Correlation coefficients to evaluate the linearty assumption.
- Limits of K_t, within 95% confidence.

7 points, the initial one with five replicates, were used. The replicates increased the accuracy of the method by increasing the number of degrees of freedom by five. (T.3.)

- Results can be found in (Table 6.3).

b) As applied to activation energy determination:

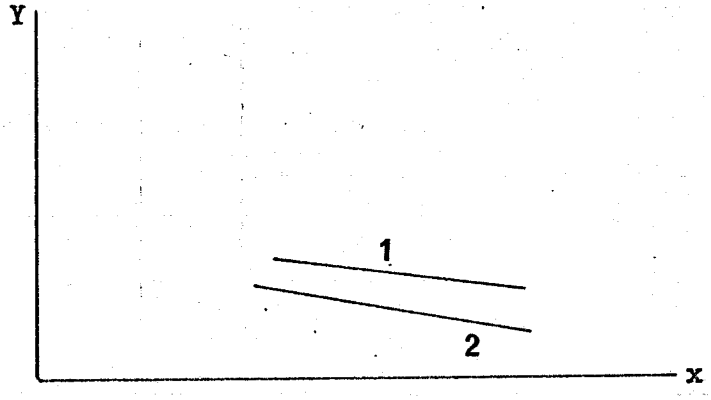
Each line is composed of three points only. Nevertheless, correlation coefficients obtained were satisfactory in asserting the linearity assumption which is considered feeble as we have just one degree of freedom. The slopes of the lines were compared to each other using a t-test (see App. VIII).

APPENDIX VIII

Comparison between slopes of two lines (V.3):

Activation energies of free radicals' decay for (c-1) and (c-2) samples at temperatures less than T_{gs}, was found to have close values. It is known that the slope of each line equals -E/R (where E is the activation energy and R = the gas constant).

A statistical test was performed to check whether it is possible to say that the two slopes are different or not.



$$Y_{(i)} = \alpha + \beta \, (x_{(i)} - \bar{x}) + \varepsilon_i \qquad 1$$

Where β is the slope and ε_i is the error.

Least squares estimate of the slope of the first line:

$$B = \frac{\sum (Y(i) - \bar{Y})(x(i) - \bar{x})}{\sum (x(i) - \bar{x})^2} \qquad 2$$

where
$$\bar{x} = \frac{x_1 + x_2 + x_3 + \ldots}{N}$$
$$= \frac{x_1 + x_2 + x_3}{3}$$

APPENDIX VII

```
        DIMENSION X(12),Y(12)
        DIMENSION AA(6),BB(6),CC(6)
C      NN IS THE NUMBER OF OBSERVATIONS .
C      IK IS THE NUMBER OF EXPERIMENTS  .
        NN=12
        IK=6
        EN=NN
        DO 2 I=8,12
        X(I)=0.0
2       CONTINUE
        DO 50 II=1,IK
        WRITE(6,120) II
        READ(5,100)(X(I),I=1,7)
        READ(5,100)(Y(I),I=1,7)
        READ(5,90)(Y(I),I=8,12)
        DO 4 J=1,12
        Y(J)=1.0/Y(J)
4       CONTINUE
        WRITE(6,100) X
        WRITE(6,100) Y
        XS=0.0
        YS=0.0
        SX2=0.0
        SY2=0.0
        SXY=0.0
        DO 10 I=1,NN
        XS=XS+X(I)
        YS=YS+Y(I)
        SX2=SX2+X(I)**2
        SY2=SY2+Y(I)**2
        SXY=SXY+X(I)*Y(I)
10      CONTINUE
        XM=XS/EN
        YM=YS/EN
        WRITE(6,102) XS,YS,SX2,SY2,SXY,XM,YM
        BETA=(EN*SXY-XS*YS)/(EN*SX2-XS**2)
        ALPHA=(YS-BETA*XS)/EN
        AA(II)=ALPHA
        BB(II)=BETA
        CC(II)=ALOG(ABS(BETA))
        V1=EN*SX2-XS**2
        V2=EN*SY2-YS**2
        R=(EN*SXY-XS*YS)/SQRT(V1*V2)
        D=2.228*BETA*SQRT((1.0-R**2)/(EN-2.0))/R
        WRITE(6,136) D
        CNF1=BETA-D
        CNF2=BETA+D
        WRITE(6,104) ALPHA,BETA
        WRITE(6,105) R
        WRITE(6,110) CNF1,CNF2
50      CONTINUE
        WRITE(6,125) AA
        WRITE(6,130) BB
        WRITE(6,135) CC
90      FORMAT(5F11.2)
100      FORMAT(7F11.2)
102     FORMAT(//29H  XS,YS,SX2,SY2,SXY,XM,YM ARE,7F13.5)
104     FORMAT(36H THE ESTIMATES OF ALPHA AND BETA ARE,2F16.5)
105     FORMAT(//14H  ---------R= ,F16.5)
```

```
      FORMAT(//30H      THE CONFIDENCE LIMITS ARE,2F16.5)
      FORMAT(//16H   C A S E  NO. ,I4)
      FORMAT(//20H  1.0/R0  -----------,6F14.5)
      FORMAT(//20H        SLOPE K  ----,6F14.5)
      FORMAT(//20H  LOG(SLOPE)  ----- ,6F14.5)
      FORMAT(//12H          D=,E16.5)
      STOP
      END
```

$$\bar{Y} = \frac{Y_1 + Y_2 + Y_3 + \ldots}{n}$$

$$= \frac{Y_1 + Y_2 + Y_3}{3}$$

The least squares estimate of the slope of the second line can be represented by a similar model.

t is given by:

$$t = \frac{(\hat{\beta}_1 - \hat{\beta}_2) - (\beta_1 - \beta_2)}{S_p\sqrt{\underbrace{\frac{1}{\sum_{i=1}^{n}(x_{(i)} - \bar{x})^2}}_{\text{1st line.}} + \underbrace{\frac{1}{\sum_{i=1}^{n}(x_{(i)} - \bar{x})^2}}_{\text{2nd line.}}}} \qquad 3.$$

S_p^2 = Pooled variance of estimate.

$$= \frac{(n-2)\,S_1^2 + (n-2)\,S_2^2}{n_1 + n_2 - 4} \qquad 4.$$

Where: $$S_1^2 = \frac{(1 - r^2)\sum(Y_{(i)} - \bar{Y})^2}{n - 2} \qquad 5.$$

and: $$r = \frac{(x_i - \bar{x})(Y_i - \bar{Y})}{\sqrt{\sum(x_i - \bar{x})^2\sum(Y_i - \bar{Y})^2}} \qquad 6.$$

S_2^2 can be represented by a similar model.

Substituting in equation 3 for the value of S_p, $\hat{\beta}_1$, $\hat{\beta}_2$, and $\sum(x_i - \bar{x})$, and putting $\beta_1 = \beta_2$ (i.e. testing the assumption that the two lines have the same slope, the obtained value of t was found = 1.396. This value is smaller than the tabulated one (4.303) for the appropriate degrees of freedom, at the 95% level. Thus, it cannot be said that the two lines have statistically different slopes at this level.

The same test was carried to compare the slopes of the two lines in (Figure 6.2"). The obtained t was found = 5.05. Thus, the latter two lines are different at this level.

APPENDIX IX

Theoretical Estimation of the Glass Transition Temperature for a Polymer-Monomer System:

A definition for the glass transition temperature can be found in (Chapter II). T_{gs} of (polystyrene-styrene) system at any composition can be theoretically derived if the glass transition temperatures, of both pure 100% polystyrene (T_{gp}) and pure styrene monomer (T_{gm}) are known. T_{gp} is a function of the polymer molecular weight. This can be represented as follows:

$$T_{gp} = T_{g\infty} - \frac{K}{M} \qquad \text{Ref.(F.3).}$$

where:

$T_{g\infty}$ = The glass transition temperature for an infinite molecular weight polymer = 373°K Ref.(B.6).

K is a constant

Kelley and Bueche (K.4) showed that K is related to the free volume per chain end (θ) by the following (see also P.38):

$$K = 2\ N \rho\, \theta/\alpha$$

where:

N = Avogrado's number

ρ = Density of the polymer given as (1.052 - 1.065) by Boundy and Boyer (B.17), and as 1.06 at room temperature by Bueche (B.20).

Θ = 65 A^{o3} for polystyrene (F.3) $\approx$ 0.6 of monomer molecular weight.

α is the expansion coefficient and may be assigned its universal value of 4.8×10^{-4} (W.6 and K.4).

Substituting by the given values in the equation:

$$T_{gp2} = 100 - 1.43 = 98.57^{\circ}C$$

$$T_{gp1} = 100 - 1.36 = 98.64^{\circ}C$$

a value of 99°C can be used for both as a reasonable approximation. Kelley and Bueche (K.4) have put forward a model relating T_{gs} to the volume fraction of polymer in the system (Q_p). This model has been proved valid and useful by Ref. (H.7) with the assumption of the additivity of the free volumes of polymer and monomer.

$$T_{gs} = \frac{\left\{ 4.8 \times 10^{-4}\, Q_p\, T_{gp} + \alpha\, m\, (1-Q_p)\, T_{gm} \right\}}{\left\{ 4.9 \times 10^{-4}\, Q_p + \alpha\, m\, (1-Q_p) \right\}}$$

where:

Q_p = polymer volume fraction.

T_{gp} = 99°C

$\alpha\, m$ = the difference between the volume expansion coefficient of monomer in melt and in the glassy state

= 11.7×10^{-4} Ref. (F.5).

T_{gm} = monomer glass transition temperature no experimental value was found. Ref. (U.1) advanced a formula relating the glass transition temperature to the molecular weight for very low values of the latter. A short extrapolation led to obtaining a value for $T_{gm} = -142^{o}C$. (See App. V.)

Assuming the additivity of polymer and monomer volume fractions, and knowing their densities at room temperature and at 100°C to be:

Styrene d_{25} = 0.9019 d_{100} = 0.8361 Ref. (B.17).

Polymer d_{25} = 1.06

d_{100} = 1.03 Ref. (B.20).

a) <u>Sample (c-1):</u>

At room temperature Q_p = 92% $Q_M = 8\%$

At 100°C Q_p = 91.6% $Q_M = 8.4\%$

An average of 91.8% Q_p and 8.2% Q_M can be conveniently used. Substituting for all the values in the T_{gs} equation we get:

T_{gs} (c-1) $\simeq$ $61.2^{o}C$

b) <u>Sample (c-2):</u>

At room temperature Q_p = 97.7% $Q_M = 2.3\%$

At 100°C Q_p = 97.5% $Q_M = 2.5\%$

Average values of Q_p are used = 97.6% Q_M = 2.4%

In the same way:

$$T_{gs}\ (c-2) \simeq 87.3^{\circ}C$$

The above calculated T_{gs} values are those for (c-1) and (c-2) just after irradiation and before annealing. As annealing progresses, T_{gs} simultaneously increases.

65.40	-27.3577	71.40	-10.6291
65.50	-27.0919	71.50	-10.3362
65.60	-26.8256	71.60	-10.0428
65.70	-26.5590	71.70	-9.7490
65.80	-26.2919	71.80	-9.4546
65.90	-26.0243	71.90	-9.1598
66.00	-25.7564	72.00	-8.8645
66.10	-25.4880	72.10	-8.5686
66.20	-25.2192	72.20	-8.2723
66.30	-24.9500	72.30	-7.9755
66.40	-24.6804	72.40	-7.6782
66.50	-24.4103	72.50	-7.3804
66.60	-24.1398	72.60	-7.0821
66.70	-23.8688	72.70	-6.7833
66.80	-23.5975	72.80	-6.4840
66.90	-23.3256	72.90	-6.1842
67.00	-23.0534	73.00	-5.8839
67.10	-22.7807	73.10	-5.5831
67.20	-22.5076	73.20	-5.2818
67.30	-22.2341	73.30	-4.9800
67.40	-21.9601	73.40	-4.6777
67.50	-21.6857	73.50	-4.3749
67.60	-21.4106	73.60	-4.0715
67.70	-21.1355	73.70	-3.7677
67.80	-20.8598	73.80	-3.4633
67.90	-20.5836	73.90	-3.1584
68.00	-20.3069	74.00	-2.8531
68.10	-20.0299	74.10	-2.5471
68.20	-19.7523	74.20	-2.2407
68.30	-19.4744	74.30	-1.9338
68.40	-19.1959	74.40	-1.6263
68.50	-18.9171	74.50	-1.3183
68.60	-18.6377	74.60	-1.0098
68.70	-18.3580	74.70	-.7008
68.80	-18.0777	74.80	-.3912
68.90	-17.7970	74.90	-.0811
69.00	-17.5159	75.00	.2295
69.10	-17.2343	75.10	.5407
69.20	-16.9523	75.20	.8523
69.30	-16.6698	75.30	1.1646
69.40	-16.3868	75.40	1.4773
69.50	-16.1034	75.50	1.7906
69.60	-15.8195	75.60	2.1044
69.70	-15.5351	75.70	2.4188
69.80	-15.2503	75.80	2.7337
69.90	-14.9650	75.90	3.0491
70.00	-14.6792	76.00	3.3651
70.10	-14.3930	76.10	3.6816
70.20	-14.1063	76.20	3.9987
70.30	-13.8192	76.30	4.3163
70.40	-13.5315	76.40	4.6345
70.50	-13.2434	76.50	4.9532
70.60	-12.9549	76.60	5.2724
70.70	-12.6658	76.70	5.5923
70.80	-12.3763	76.80	5.9126
70.90	-12.0863	76.90	6.2336
71.00	-11.7958	77.00	6.5550
71.10	-11.5049	77.10	6.8771
71.20	-11.2134	77.20	7.1997
71.30	-10.9215	77.30	7.5228

77.40	7.8466	83.40	28.3580
77.50	8.1709	83.50	28.7190
77.60	8.4957	83.60	29.0807
77.70	8.8211	83.70	29.4430
77.80	9.1471	83.80	29.8060
77.90	9.4737	83.90	30.1697
78.00	9.8008	84.00	30.5341
78.10	10.1285	84.10	30.8991
78.20	10.4568	84.20	31.2648
78.30	10.7856	84.30	31.6312
78.40	11.1151	84.40	31.9983
78.50	11.4451	84.50	32.3660
78.60	11.7757	84.60	32.7345
78.70	12.1068	84.70	33.1036
78.80	12.4386	84.80	33.4734
78.90	12.7709	84.90	33.8439
79.00	13.1039	85.00	34.2151
79.10	13.4374	85.10	34.5869
79.20	13.7715	85.20	34.9595
79.30	14.1062	85.30	35.3328
79.40	14.4415	85.40	35.7067
79.50	14.7774	85.50	36.0814
79.60	15.1138	85.60	36.4567
79.70	15.4509	85.70	36.8328
79.80	15.7886	85.80	37.2096
79.90	16.1269	85.90	37.5871
80.00	16.4658	86.00	37.9653
80.10	16.8052	86.10	38.3442
80.20	17.1453	86.20	38.7238
80.30	17.4860	86.30	39.1041
80.40	17.8273	86.40	39.4852
80.50	18.1692	86.50	39.8670
80.60	18.5118	86.60	40.2495
80.70	18.8549	86.70	40.6327
80.80	19.1987	86.80	41.0166
80.90	19.5431	86.90	41.4013
81.00	19.8880	87.00	41.7867
81.10	20.2337	87.10	42.1728
81.20	20.5799	87.20	42.5597
81.30	20.9268	87.30	42.9473
81.40	21.2742	87.40	43.3357
81.50	21.6224	87.50	43.7248
81.60	21.9711	87.60	44.1146
81.70	22.3205	87.70	44.5052
81.80	22.[illegible]05	87.80	44.8965
81.90	23.[illegible]11	87.90	45.2886
82.00	23.3724	88.00	45.6814
82.10	23.7243	88.10	46.0750
82.20	24.0768	88.20	46.4693
82.30	24.4300	88.30	46.8644
82.40	24.7839	88.40	47.2603
82.50	25.1384	88.50	47.6569
82.60	25.4935	88.60	48.0543
82.70	25.8493	88.70	48.4524
82.80	26.2[illegible]57	88.80	48.8514
82.90	26.5628	88.90	49.2511
83.00	26.9205	89.00	49.6515
83.10	27.2789	89.10	50.0528
83.20	27.6379	89.20	50.4548
83.30	27.9976	89.30	50.8576

89.40	51.2612
89.50	51.6655
89.60	52.0707
89.70	52.4766
89.80	52.8834
89.90	53.2909
90.00	53.6992
90.10	54.1084
90.20	54.5183
90.30	54.9290
90.40	55.3406
90.50	55.7529
90.60	56.1661
90.70	56.5801
90.80	56.9948
90.90	57.4105
91.00	57.8269
91.10	58.2441
91.20	58.6622
91.30	59.0811
91.40	59.5008
91.50	59.9214
91.60	60.3428
91.70	60.7650
91.80	61.1881
91.90	61.6120
92.00	62.0368
92.10	62.4624
92.20	62.8889
92.30	63.3162
92.40	63.7444
92.50	64.1734
92.60	64.6033
92.70	65.0341
92.80	65.4657
92.90	65.8982
93.00	66.3315
93.10	66.7658
93.20	67.2009
93.30	67.6369
93.40	68.0737
93.50	68.5115
93.60	68.9501
93.70	69.3897
93.80	69.8301
93.90	70.2714
94.00	70.7136
94.10	71.1567
94.20	71.6008
94.30	72.0457
94.40	72.4915
94.50	72.9383
94.60	73.3859
94.70	73.8345
94.80	74.2840
94.90	74.7344
95.00	75.1858
95.10	75.6380
95.20	76.0913
95.30	76.5454
95.40	77.0005
95.50	77.4565
95.60	77.9135
95.70	78.3714
95.80	78.8302
95.90	79.2900
96.00	79.7508
96.10	80.2125
96.20	80.6752
96.30	81.1389
96.40	81.6035
96.50	82.0690
96.60	82.5356
96.70	83.0031
96.80	83.4716
96.90	83.9411
97.00	84.4116
97.10	84.8831
97.20	85.3555
97.30	85.8290
97.40	86.3035
97.50	86.7789
97.60	87.2554
97.70	87.7328
97.80	88.2113
97.90	88.6908
98.00	89.1713
98.10	89.6528
98.20	90.1354
98.30	90.6189
98.40	91.1035
98.50	91.5892
98.60	92.0758
98.70	92.5636
98.80	93.0523
98.90	93.5421
99.00	94.0330
99.10	94.5249
99.20	95.0178
99.30	95.5119
99.40	96.0070
99.50	96.5031
99.60	97.0003
99.70	97.4986
99.80	97.9980
99.90	98.4985
100.00	99.0000

APPENDIX X

HEWLETT hp PACKARD
ANALYTICAL INSTRUMENTS

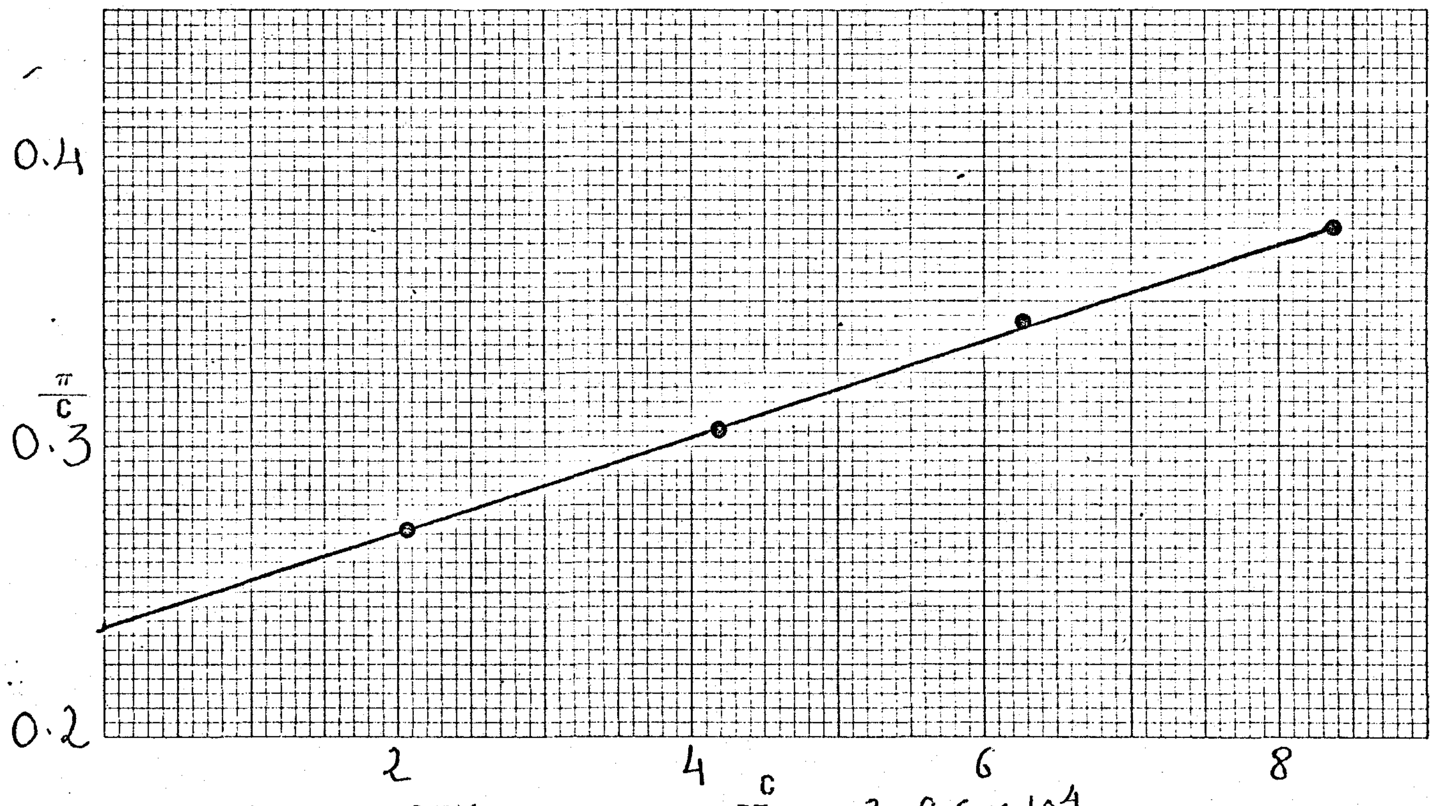
LABORATORY WORK SHEET

SERIES 500 MEMBRANE OSMOMETERS

Sample (C-1) [172-40]   Solvent TOLUENE M_n = **124,900**

Temperature 30 °C   Membrane   Instrument 502 OSM.

	25%	50%	75%	100%			Remarks
Concentration, C	2.095	4.19	6.28	8.38			
Solvent Pressure (P_0)	18.06	18.06	18.08	18.04	18.06	AV.	
Sample Pressure	18.63	19.35	20.24	21.18			
Sample Pressure	18.63	19.33	20.18	21.22			
Average Pressure (P)	18.63	19.34	20.21	21.20			
$\pi = P - P_0$	0.57	1.28	2.15	3.14			
π/C	0.272	0.305	0.342	0.375			



$(\pi/C)_{c\to 0}$ from graph 0.237   RT = 2.96×10^4

Molecular Weight = $\frac{RT}{(\pi/C)_{c\to 0}}$ = $\frac{2.96 \times 10^4}{0.237}$ = 124.9×10^3

Analyst: Date: No:

Company: Address:

Part No. 9320-1106
Printed in U.S.A.

BIBLIOGRAPHY

(A.1) Abraham, R. J., Melville, H. W., Overall, D. W., and Whiffen, D. H., Trans. Far. Soc., 54, 113 (1958).

(A.2) Abraham, R. J., Overall, D. W., and Whiffen, D. H., Arch. Sci., 10, 84, (1957).

(A.3) Abraham, R. J., and Whiffen, D. H., Trans. Far. Soc., 54, 1291 (1958).

(A.4) Assenheim, H. M., "Introduction to Electron Spin Resonance", Plenum Press, New York (1967).

(A.5) Aoki, A., and Sewada, S., Rep. on Prog. in Pol. Phys. in Japan, 10, 261 (1967).

(A.6) Ard, W. B., Shields, H., and Gardy, W., J. Chem. Phys., 23, 1727 (1955).

(A.7) Atherton, N. M., Melville, H., and Whiffen, D. H., J. Pol. Sci., 34, 199 (1959)

(B.1) Bamford, C. H., Barb, W. G., Jenkins, A. D., and Onyon, P. F., "The Kinetic of Vinyl Polymerization By Radical Mechanisms", Butterworths Pub., London (1958).

(B.2) Bamford, C. H., and Dewar, M. J., Naturem 157, 845 (1946).

(B.3) Bamford, C. H., and Dewar, M. J., Proc. Roy. Soc.,(London) A, 192, 309 (1948).

(B.4) Bamford, C. H., and Jankins, A. D., Proc. Roy. Soc.(London) A, 216, 515 (1953).

(B.5) Bamford, C. H., and Jenkins, A. D., Proc. Roy. Soc., (London), A, 228, 220, (1955).

(B.6) Bandrup, J., and Immergut, E. H., "Polymer Handbook", Interscience

Publishers, New York,(1966).

(B.7) Bass, A. M., and Broida, H. P., "Formation and Trapping of Free Radicals", Academic Press, New York (1960).

(B.8) Bengaugh, W. I., and Melville, H. W., Proc. Roy. Soc. (London), A, 230, 429 (1955).

(B.9) Benson, S. W., and North, A. M., J. Amer. Chem. Soc., 81, 1339 (1959).

(B.10) Benson, S. W., and North, A. M., J. Amer. Chem. Soc., 84, 935 (1962).

(B.11) Bertthelot, M., Bull. Soc. Chim., (2), 6, 294 (1866).

(B.12) Bielski, B. H. J., and Gebicki, J. M., "Atlas of Electron Spin Resonance Spectra", Academic Press, New York (1967).

(B.13) Billmeyer, F. W., "Text Book of Polymer Science", Interscience Publishers, New York (1962).

(B.14) Blyth, J., and Hoffman, A. W., Annalen, 53, 292 (1945).

(B.15) Blyth, J., and Hoffman, A. W., Annalen, 53, 314 (1945).

(B.16) Bonastre, M., J. Pharm. Chim., 17, 338 (1831).

(B.17) Boundy, and Boyer, "Styrene, Its Polymers, Copolymers and Derivatives".

(B.18) Bowden, M.J., and O'Donnell, J. H., J. Pol. Sci., A-1, 7, 1657 (1969).

(B.19) Bresler, S. E., Kazbekov, E. N., and Saminski, E. M., Vysokomolekularnye Soedinenia, 1, 132,(1959).

(B.20) Bueche, F., "Physical Properties of Polymers", Interscience Publishers, New York (1962).

(B.21) Burnette, G. H., "Mechanism of Polymer Reactions", Interscience Publishers, New York (1954).

(B.22) Burton, M., Disc. Far. Soc., 12, 317 (1952).

(C.1) Campbell, D., Araki, K., and Turner, D. T., J. Pol. Sci., 4, 2597 (1966).

(C.2) Catherines, S., and Chen, H., J. Pol Sci., 58, 389 (1962).

(C.3) Catherines, S., Chen, H., and Stamm, R., J. Pol. Sci., 58, 369 (1962).

(C.3) Chapiro, A., Compt. Rend., 228, 1490 (1949).

(C.4) Chapiro, A., "Radiation Chemistry of Polymeric Systems", Interscience Publishers (1962).

(C.5) Chapiro, A., Cousin, C., Landler, Y., and Magat, M., Rec. Trav. Chim., 68, 1037 (1949).

(C.6) Chapiro, A., Magat, M., Sebban, J., and Wahl, P., Inter Symp. Macromal. Chem., Milan-Torino, (1954), - Ricerca Sci. Suppl., A, 73 (1955).

(C.7) Chapiro, A., and Nakashio, S., J. Chim. Phys., 63, 1031 (1966).

(C.8) Chapiro, A., and Wahl, P., Compt. Rend., 238, 1803,(1954).

(C.9) Charlesby, A., Proc. Roy. Soc. (London), A, 215, 187 (1952).

(C.10) Charlesby, A., J. Pol. Sci., 11, 513 (1953).

(C.11) Charlesby, A., Rep. Prog. Phys., 28, 462 (1965).

(C.12) CH'Ienjen-Yuan, "Determination of Molecular Weights of high Polymers, IPST, Oldbourne Press, London

(C.13) Collinson, E., Disc. Far. Soc., 12, 125 (1952).

(C.14) Crank, J., and Park, G. S., "Diffusion in Polymers", Academic Press, London (1968).

(D.1) Dean, D., "Radiation Induced Polymerization of Styrene", M. Eng. Thesis, McMaster University, (1968).

(D.2) Deutsch, K., Hoff, E. A. W., and Reddish, W., J. Pol. Sci., 13, 565 (1954).

(D.3) Dole, M., and Keeling, C. D., J. Amer. Chem. Soc., 75, 6082,(1953).

(D.4) Dole, M., Keeling, C. D., and Rose, D. G., J. Amer. Chem. Soc., 76, 4304.(1954).

(E.1) Ewart, R. H., Abstracts of Papers presented at the 111th meeting of the American Chemical Society, Atlantic City, N. J., April 14-18 (1947).

(F.1) Florin, R. E., Wall, L. A., and Brown, D. W., Trans. Far. Soc., 2, 1304,(1960).

(F.2) Flory, P. J., J. Amer. Chem. Soc., 59, 241 (1937).

(F.3) Flory, P. J., and Fox, T. G., J. Appl. Phys., 21, 587,(1950).

(F.4) Fox, T. G., and Flory, P. J., J. Pol. Sci. 14, 315 (1954).

(F.5) Fox, T. G., and Loshaek, S., J. Pol. Sci., 15, 371 (1955).

(F.6) Fraintel, Hirshan, , and Walling , J. Amer. Chem. Soc., 76, 3606,(1954).

(F.7) Fuji, S., Bull. Chem. Soc., Japan, 27, 216 (1954).

(G.1) Golden, S., J. Chem. Phys., 29, 61 (1958).

(H.1) Hamielec, A. E., and Wilson, D., unpublished data, McMaster University (1969).

(H.2) Hedvig, P., J. Pol. Sci., A-1, 7, 1145 (1969).

(H.3) Hodgins, J. W., and Sood, S., McMaster University (1969) (to be published).

(H.4) Hodgins, J. W., Werezak, G. N., and Ross, S. L., Can. J. Chem. Eng., 43, 117 (1965).

(H.5) Hopwood, F. L., Brit, J. Radiol., 13, 221 (1940).

(H.6) Hopwood, F. L., and Phillips, J. J., Proc. Phys. Soc., (London), 50, 438 (1938).

(H.7) Horie, K., Mita, I., and Kambe, H., J. Pol. Sci. A-1, 6, 2663
((1968)

(H.8) Howard, R. N., Trans. Far. Soc., 46, 204 (1950).

(H.9) Huang, R. Y., Westlake, J. F., and Sherma, S. C., J. Pol. Sci., A-1

7, 1729 (1969).

(H.10) Hui, A.,"Unpublished Observations", McMaster University (1969).

(I.1) Ingram, D. J. E., "Free Radicals as studied by E.S.R.", Butterworths, London (1958).

(I.2) Ingram, D. J. E., Symonds, M. C. R., and Townsend, M. J., Trans. Far. Soc., 53, 1914 (1957).

(I.3) Isenbrand, J. E., and Eich, H. W., Z. Anal. Chem., 175, 4 (1966).

(J.1) Jackson, J. L., and Montroll, E. W., J. Chem. Phys., 28, 1101 (1958).

(K.1) Kaetsu, I., Tsuji, K., Hayashi, K., and Okamura, S., J. Pol. Sci., A-1, 5, 1899 (1967).

(K.2) Kagiya, T., Izu, M., Kawai, S., and Fukui, K., J. Pol. Sci., A-1, 5, 1415 (1967).

(K.3) Kampbell, D., Araki, K., and Turner, D. T., J. Pol. Sci., 4, 2597 (1966).

(K.4) Kelley, F. N., and Bueche, F., J. Pol. Sci., 1, 549 (1961).

(K.5) Kells, D. J. C., Koike, M., and Guillet, J. E., J. Pol. Sci., A-1, 6, 595 (1968).

(K.6) Kraemer, E. O., and Lansing, W. D., J. Amer. Chem. Soc., 57, 1369 (1935).

(K.7) Kronstein, A., Ber., 35, 4153 (1902).

(K.8) Kruyt., Colloid Science (Elsevier Publishing Company), 2, 60 (1949).

(L.1) Landler, Y., Thesis, University of Paris, (1952).

(L.2) Lawton, E. J., Bueche, A. M., and Balwit, J. S., Nature, 172, 176 (1953).

(L.3) Lawton, E. J., Grubb, W. T., and Balwit, J. S., J. Pol. Sci., 19, 455 (1956).

(L.4) Levenspiel, O., "Chemical Reaction Engineering", John Wiley, New York (1962).

(L.5) Lewis, G. N., and Lipkin, D., J. Amer. Chem. Soc., 64, 2801 (1942).

(M.1) MacKay, M. H., and Melville, H. W., Trans. Far. Soc., 45, 323 (1949).

(M.2) Magat, M., Chapiro, A., Cousin, C., and Landler, Y., Rec. Trave. Chim. Pays-Bas, 68, 1037 (1949).

(M.3) Magat, M., and Landler, Y., Bull. Soc. Chim. Belg., 57, 381 (1948).

(M.4) Matheson, M. S., Aver. E. E., Bevilaqua, E. B.,,and Hart, E. J., J. Amer. Chem. Soc., 73, 1700 (1951).

(M.5) McMillan, W. G., and Mayer, J. E., J. Chem. Phys., 13, 276 (1945).

(M.6) Medvedev, S. S., Koritskaya, O., and Alekseyeva, E., Zuhr. Fiz. Khim., 17, 39 (1943).

(M.7) Melville, H. W., Z. Elektrochem., 60, 276 (1956).

(M.8) Michel, R. E., Chapman, F. W., and Mao, T. J., J. Pol. Sci., A-1, 5, 677 (1967).

(N.1) Nara, S., Kashiwatara, H., and Sohma, J., Rep. Prog. Pol. Phys., Japan, 10, 479 (1967).

(N.2) Nara, S., Shimada, S., Kashiwabara, H., and Sohma, J., Rep. Prog. Pol. Phys., Japan, 11, 465, (1968).

(N.3) North, A. M., and Reed, G. A., J. Pol. Sci., A-1, 1311,(1963).

(O.1) Ohnishi, S. I., and Nitta, I., J. Pol. Sci., 38, 451 (1959).

(O.2) Okamura, S., Higashimura, T., and Futami, S., Isotopes and Radiations, Japan, 1, 216 (1958).

(O.3) Ostromislensky, I. J., J. Russ, Phys. Chem. Soc., 44, 204 (1911).

(P.1) Pepper, D. C., Sci. Proc. Roy. Soc., Dublin, 25, 239 (1951).

(P.2) Plesh, P. H., "The Chemistry of Cationic Polymerization", The McMillan

Company, New York (1963).

(P.3) Potter, R. C., Johnson, C. L., Metz, D. J., and Brettan, R.H., J. Pol. Sci., A-1, 4, 419 (1966).

(P.4) Powles, J. G., J. Pol. Sci. 22, 79, (1956).

(P.5) Prevot, A., Compt. Rend., 230, 288 (1950).

(P.6) Pryor, W. A.,

(R.1) Rabinowitch, E., Trans. Far. Soc., 33, 1225 (1937).

(R.2) Ragovir, Z. A., and Tsaplin, L. A., J. App. Chem., (U.S.S.R.), 20, 875 (1947).

(R.3) Roche, A., and Price, C. E., The Dow Chemical Company, unpublished observations.

(R.4) Robertson, E. R., Trans. Far. Soc., 52, 426 (1956).

(S.1) Scheilds, H., Ard, W. D., and Gordy, W., Amer. Phys. Soc., 2, 227 (1952).

(S.2) Schneider, E.E., Far. Soc. Disc., 19, 158 (1955).

(S.3) Schneider, E. E., Day, M. J., and Stein, G., Nature, 168, 645 (1951).

(S.4) Schulz, G. V., Z. Phys., Chem., (Frankfurt), 8, 290, (1956).

(S.5) Schulz, G. V., and Husemann, E., Z.Phys. Chem., B-34, 187 (1936).

(S.6) Sears, W. C., and Parkinson, W. W., J. Pol. Sci., 21, 325 (1956).

(S.7) Seitzer, W.H., and Tobolsky, A. V., J. Amer. Chem. Soc., 77, 2687, (1955).

(S.8) Sheinker, A. P., Yakovleva, M. K., Kristalnyi, E. V., and Abkin, A. D., Doklady Akad. Nark. U.S.S.R., 124, 632 (1959).

(S.9) Shibayama, K., and Lisaka, K., Rep. Prog. Pol. Phys., Japan, 10, 393, (1967).

(S.10) Shida, S., Higushi, J., Kusaka, R., and Miyamae, T., Read at the symposium on radiation chemistry sponsored by the Chemical Society of Japan, November (1958).

(S.11) Shultz, A. R., Roth, P. I., and Rathmann, G. B., J. Pol. Sci., 22, 495, (1956).

(S.12) Simon, E., Annalen, 31, 265 (1839).

(S.13) Sisman, O., and Bopp, C. D., In "ONR-NRL Symposium on Radiation effects on dielectric materials" December 14-15 (1954).

(S.14) Spencer, R. S., and Williams, , J. Colloid. Sci., 4, 247 (1949).

(S.15) Spinks, J. W. T., and Woods, R. J., "An Introduction to radiation Chemistry" John Wiley, New York (1964).

(S.16) Standinger, H., Ber.,53, 1073 (1926).

(S.17) Steacie, E.W. R., "Atomic and Free Radical Reactions", Reinhold, New York, (1954).

(S.18) Swallow, A. J., "Radiation Chemistry of Organic Compounds", Pergamon Press, London, (1960).

(T.1) Tabata, Y., Shu, S., and Oshima, K., Rep. Prog. Pol. Phys., Japan, 10, 491, (1967).

(T.2) Tamura, N., Toyota, N., and Machi, S., Rep. Prog. Pol. Phys., Japan, 11, 481 (1968).

(T.3) TiKu, M. L., "Basic Statistics for Engineers", course notes (No. 7511), Appl. Math Dept. McMaster University, 1970.

(T.4) Tobolsky, A. V., "Properties and Structure of Polymers", Johm Wiley, New York (1962).

(T.5) Tromsdorff, "Colloquium on high Polymers", Freiburg (1944).

(U.1) Ueberreiter, K., and Kanig, G., J. Colloid. Sci., 7, 569 (1953).

(V.1) Vaughan, M. F., Trans. Far. Soc., 48, 576 (1952).

(V.2) Veda, H., Kuri, Z., and Shida, S., J. Chem. Phys., 36, 1676, (1962).

(V.3) Volk, W., "Applied Statistics for Engineers", McGraw Hill, Toronto (1958).

(W.1) Wall, L. A., and Brown, D.W., J. Phys. Chem., 61, 129 (1957).

(W.2) Walling, G. T., Briggs, E. R., and Mayo, F. R., J. Amer. Chem. Soc., 68, 1145 (1946).

(W.3) Werezak, G. M. Eng. Thesis, McMaster University (1963).

(W.4) Werezak, G., Ph.D., Thesis, McMaster University (1966).

(W.5) Whyte, G. N., "Principles of Radiation Dosimetry", John Wiley, New York (1959).

(W.6) Williams, M. L., Landel, R. F., and Ferry, J. D., J. Amer. Chem. Soc., 77, 3701 (1955).

(W.7) Wyard, S.J., J. Sci. Instr., 42, 769 (1965).