

THE UNIVERSITY OF MICHIGAN  
INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

POLAR EFFECTS IN THE RADIATION  
CHEMISTRY OF p-SUBSTITUTED POLYSTYRENES

Vinicio Serment

A dissertation submitted in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy in the  
University of Michigan  
1961

February 1961  
IP - 498

Doctoral Committee:

Professor Henry J. Gomberg, Chairman  
Doctor William J. Burlant  
Assistant Professor Bernard A. Galler  
Professor William Kerr  
Associate Professor Wayne W. Meinke  
Professor Richard K. Osborn

## ACKNOWLEDGMENTS

The author expresses his gratitude to the Scientific Laboratory of the Ford Motor Company for its help throughout this work: special thanks are due to Dr. W. J. Burlant for his guidance, interest and understanding, to Mr. C. R. Taylor for the preparation of the polymers used in this study, and to Mr. J. Neerman for his valuable help with the mass spectrometric analyses.

The author is indebted also to the members of his Doctoral Committee for stimulating discussions.

The use of the facilities of the Phoenix Memorial Laboratory and the help from the members of its staff is gratefully acknowledged.

The financial support of the University of Mexico, the Mexican Nuclear Energy Commission and the Mexican Light and Power Company throughout the author's studies is also gratefully acknowledged.

Thanks are tendered also to Mrs. Marvin Leech and Mrs. Ivan Zeeb for the preparation of the first draft of this work.

Finally, sincere thanks are due to the Industry Program of the College of Engineering for the reproduction of this thesis.

## TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS.....	ii
LIST OF TABLES.....	iv
LIST OF FIGURES.....	v
I INTRODUCTION.....	1
A. Statement of Problem.....	1
B. Glossary of Terms Used in Polymer and Radiation Chemistry.....	2
C. Effects of Ionizing Radiation on Polymers.....	5
1. General.....	5
2. Radiation Effects in Amorphous Polystyrene.....	10
3. Steric and Polar Effects.....	16
II EXPERIMENTAL PROCEDURES.....	25
A. Preparation of Vinyl Monomers.....	25
B. Preparation of Polymers.....	26
C. Sample Irradiations.....	27
D. Gas Evolution Measurements.....	29
E. Molecular Weight Data and G(Crosslink).....	32
III RESULTS AND DISCUSSION.....	37
A. Preliminary Experiments.....	37
1. Effect of Impurities.....	37
2. Dose Rate Dependence.....	39
B. Hydrogen Yields.....	40
1. Temperature Effects.....	44
2. Mechanism of Gas Formation.....	44
a. Hydrogen.....	44
b. Methane.....	48
C. Crosslinking.....	48
1. Resonance Effects.....	48
2. Poly-p-Bromo- and Poly-p-Chlorostyrenes.....	69
3. Temperature Dependence of Crosslinking.....	71
D. Dose for Incipient Gelation.....	72
IV SUMMARY OF CONCLUSIONS.....	77
BIBLIOGRAPHY.....	79

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	p-substituted Polystyrenes Studied.....	2
II	Effects of Ionizing Radiation on Polymers.....	17
III	Values of $\sigma$ for Substituents in the Para Position.....	21
IV	Revised $\sigma$ Constants ( $\sigma^+$ ) to Take Into Account Resonance Effects.....	22
V	Intrinsic Viscosity-Number Average Molecular Weight Data for Some Polystyrenes.....	35
VI	Effect of Oxygen Atoms on the Radiation Chemistry of Polystyrenes.....	37
VII	Some Average Bond Energies.....	39
VIII	Mass Spectrometric Analysis of Gases Produced From the $\gamma$ -Irradiation of p-Substituted Polystyrenes.....	40
IX	$G(H_2)$ and $G(CH_4)$ Values for the $\gamma$ -Irradiation of p- Substituted Polystyrenes.....	41
X	$\gamma$ -Irradiation of Deuterated Polystyrenes.....	42
XI	Effect of Dose on $G(\text{Crosslink})$ for p-Substituted Polystyrenes.....	63
XII	Huggins' Constant, $k'$ , for the $\gamma$ -Irradiation of Poly-p-Methylstyrene and Poly-p-Methoxystyrene.....	64
XIII	Dependence of $G(\text{Crosslink})$ and the Dose for Incipient Gelation, $D$ , on the p-Substituent.....	74

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Sealing Assembly for the $\gamma$ -Irradiation of the p-Substituted Polystyrenes.....	28
2	Teflon Gasketed Compression Seal Used to Seal Ampules to Mass Spectrometer.....	31
3	Molecular Model of Poly-p-Bromostyrene Indicating the Absence of Steric Hindrance in the Backbone by the p-Substituent.....	38
4	Ultraviolet Absorption Spectra of Unirradiated and Irradiated Polymer Films.....	46
5	Dependence of $[\eta]$ on Total Dose for $\gamma$ -Irradiated Poly-p-Methoxystyrene, at 25°C.....	49
6	Dependence of $[\eta]$ on $\gamma$ -Irradiated Poly-p-Methoxystyrene on the Temperature of the Irradiation, at a Total Dose of $4.5 \times 10^6$ R.....	50
7	Dependence of $[\eta]$ on Total Dose for $\gamma$ -Irradiated Poly-p-Methylstyrene, at 25°C.....	51
8	Dependence of $[\eta]$ of $\gamma$ -Irradiated Poly-p-Methylstyrene on the Temperature of Irradiation, at a Total Dose of $4.5 \times 10^6$ R.....	52
9	Dependence of $[\eta]$ of $\gamma$ -Irradiated Polystyrene on the Total Dose, at 25°C.....	53
10	Dependence of $[\eta]$ of $\gamma$ -Irradiated Polystyrene on the Temperature of the Irradiation, at a Total Dose of $4.5 \times 10^6$ R.....	54
11	Dependence of $[\eta]$ of $\gamma$ -Irradiated Poly-p-Chlorostyrene on the Total Dose, at 250°C.....	55
12	Dependence of $[\eta]$ of $\gamma$ -Irradiated Poly-p-Chlorostyrene on the Temperature of the Irradiation, at a Total Dose of $2.8 \times 10^6$ R.....	56
13	Dependence of $[\eta]$ of $\gamma$ -Irradiated Poly-p-Bromostyrene on the Temperature of the Irradiation, at a Total Dose of $0.05 \times 10^6$ R.....	57

LIST OF FIGURES (CONT'D)

<u>Figure</u>		<u>Page</u>
14	Dependence of $[\eta]$ of $\gamma$ -Irradiated Poly-p-Bromostyrene on the Temperature of the Irradiation, at a Total Dose of $0.93 \times 10^6$ R.....	58
15	Dependence of $[\eta]$ of $\gamma$ -Irradiated Poly-p-Cyanostyrene on the Total Dose, at $25^\circ\text{C}$ .....	59
16	Dependence of $[\eta]$ of $\gamma$ -Irradiated Poly-p-Cyanostyrene on the Temperature of the Irradiation, at a Total Dose of $4.5 \times 10^6$ R.....	60
17	Dependence of $[\eta]$ of $\gamma$ -Irradiated Poly-p-Nitrostyrene on the Total Dose, at a Temperature of $25^\circ\text{C}$ .....	61
18	Dependence of $[\eta]$ of $\gamma$ -Irradiated Poly-p-Nitrostyrene on the Temperature of the Irradiation, at a Total Dose of $4.5 \times 10^6$ R.....	62
19	$[\eta]$ -Dose Curves Used to Determine the Dose for Incipient Gelation.....	76

## I. INTRODUCTION

### A. Statement of Problem

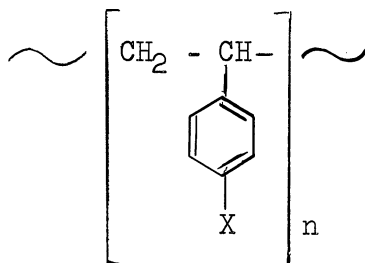
Studies of the interaction of ionizing radiation with organic polymers began as early as the 1930's, when it was found that such radiations produced profound changes in the melting characteristics of the absorber. In the last ten years, with the advent of high energy sources, renewed interest in this area was noted, although most of the published investigations describe only the industrially important gross changes induced by pile- and  $\gamma$ -radiations.

At present there is no theory which can predict the nature, number, spatial distribution and fate of both the primary and secondary active species formed when a polymer is irradiated. Nevertheless, most of the radiation induced changes of crosslinking, degradation, unsaturation, oxidation and gas formation, can be explained qualitatively in terms of simple free radical reactions familiar to organic chemists, and like the latter should be sensitive to the steric and polar environment about the susceptible (or reacting) carbon atom. The literature describes a few efforts to elucidate the role of the steric configuration of the polymer chain.

The object of this work is the study of polar effects in the radiation chemistry of polystyrenes. More precisely, the electronic environment about the backbone carbon atoms has been altered by introducing electronegative or electropositive substituents in the chain, Table I summarizes the polymers studied. The susceptibility of these polymers to  $\gamma$ -initiated bond cleavage was determined from (1) mass spectrometric



TABLE I  
p-SUBSTITUTED POLYSTYRENES STUDIED



where X = OCH<sub>3</sub>, CH<sub>3</sub>, H, Cl, Br, CN, NO<sub>2</sub>

and n ≈ 2500 .

examination of the effluent gases (2) viscometrical molecular weight determinations and (3) doses for incipient gelation. From these data, G-values for hydrogen formation and G-values for crosslinking have been calculated. The results of these studies, together with data reported by others on radical reactions in solutions and in the gas phase suggest that free radical species formed early in the reaction are responsible for the major radiation effects observed, i.e., hydrogen formation and crosslinking, and that the latter effects in fact can be interpreted in terms of the stability of the intermediate polymer radical formed as a result of the  $\gamma$ -irradiation (Sections III-B and III-C).

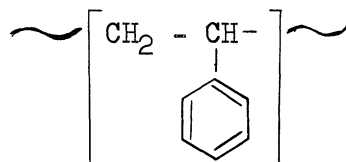
B. Glossary of Terms Used in  
Polymer and Radiation Chemistry

This section defines the more general terms employed in this work; specific equations or more specialized concepts are discussed more fully in the section in which they are noted.

POLYMER CHEMISTRY

Linear Polymer

A high molecular weight, chain-like molecule comprised of repeating low molecular weight units. The repeating unit in linear polystyrene, for example, is the



group; for the polymers used in this study,  $n \cong 2500$ .

The present investigation is concerned exclusively with vinyl polymers produced via free radical initiated addition of monomer units in homogeneous solution. Polymers prepared in this way usually are amorphous, i.e., there is no regularity or order of the polymer chains with respect to adjacent chains or with respect to sequence lengths (a few monomer units) on the same chain. X-ray diffraction patterns of such materials consist only of ill-defined halos.

Copolymer

A chain containing two or more different monomer units.

Degree of Polymerization

Number of monomer units in a polymer chain.

Crosslinks

Chemical bonds between adjacent polymer chains.

Scission

Main chain bond cleavage.

Gel

Insoluble polymer.

Molecular Weights

As normally prepared, a polymer contains chains of varying molecular weight. Several "averages" of the molecular weight thus are possible:

$$\text{Number average molecular weight} = M_n = \frac{\sum n_M M}{\sum n_M}$$

$$\text{Weight average molecular weight} = M_w = \frac{\sum n_M M^2}{\sum n_M M}$$

where  $n_M$  = the number of molecules possessing molecular weight  $M$ .

### Intrinsic Viscosity

A convenient method of measuring average molecular weights depends on the viscosity of dilute solutions of the polymer. The intrinsic viscosity

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_s - \eta_0}{c \eta_0}$$

where  $c$  is the concentration and  $\eta_s$  is the viscosity of the polymer solution;  $\eta_0$  is the viscosity of the solvent. For most polymers the weight average molecular weight or the number average molecular weight can be related to the intrinsic viscosity according to the following empirically derived expression:

$$[\eta] = KM^\alpha$$

where  $K$  and  $\alpha$  are constants for a particular system and depend on the chemical structures of the polymer and solvent and on the temperature. For polymers for which  $K$  and  $\alpha$  are known, therefore, a determination of  $[\eta]$  leads immediately to an average molecular weight.

### Free Radical

A molecule containing an unpaired electron.

### Steric Effects

Changes in the course of a reaction resulting from the presence of bulky substituent at or near the reactive site.

## RADIATION CHEMISTRY

Curie	That quantity of radioactive material which undergoes $3.700 \times 10^{10}$ disintegrations/sec.
Dose	The energy absorbed per unit mass of irradiated material.
Rad	A unit of dose of any radiation which results in the absorption of 100 ergs of energy/g of absorber.
Dose Rate	The rate of energy absorption/unit mass of irradiated material; rads/unit time.
Energy yield (G-value)	The number of atoms or molecules produced (or used up) in an irradiated system for each 100 ev of energy absorbed.
First Ionization Potential	The minimum energy required to ionize a neutral molecule. For low molecular weight saturated hydrocarbons (propane, e.g.) the value is equal to 11 ev. In organic molecules, bond energies (E) are lower than the ionization energies; thus, the E for C-C is 5.1 ev and E for C-H is 4.3 ev.

### C. Effects of Ionizing Radiation on Polymers<sup>(1,2)</sup>

#### 1. General

Ionizing radiation includes fast electrons, fast protons, neutrons and  $\alpha$  particles, and the electromagnetic radiation of short wave length- X-rays and  $\gamma$ -rays. The energies of these radiations are above about 100 ev.

All high energy radiations interact with the electrons and/or the nuclei of the exposed system so that free electrons, ionized and excited

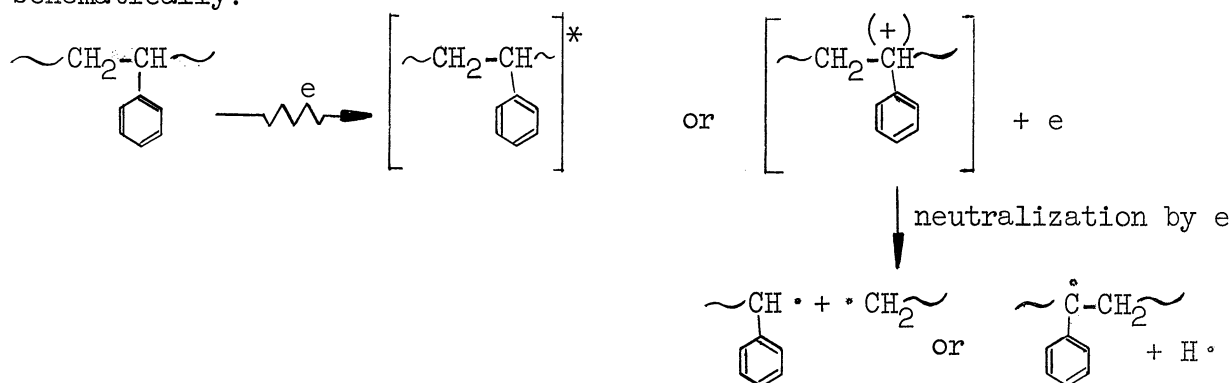
atoms or molecules are produced; changes in nuclear structure also can occur. If we restrict the discussion to radiation effects on organic polymers (which can be considered a chain of  $-\text{CH}_2$  groups) the most significant differences between these radiations depend on the rate of energy loss per unit length of path traveled in the material. This determines the penetration of the incident beam, the density, and the distribution of the active species formed about each incident photon or particle.

#### Electrons ( $\beta$ -Rays)

The absorption by organic molecules of electrons of energies normally used in radiation studies (of the order of 1 Mev) leads to excitation and ionization of the orbital electrons. The strong electrical repulsive or attractive forces present in the system result in a higher rate of energy deposition, and greater scattering of the electrons, i.e., lower effective penetration per unit path length compared to the  $\gamma$ - and X-rays. Continued excitation and ionization by the energetic electrons produced gives rise to electron "showers" in the irradiated medium. Each incident electron in a 1 Mev beam produces about ten secondary electrons of energies of several Kev, so that the noted chemical effects of the primary beam are negligible.

Both the positive ion and the excited molecule initially formed are unstable states, and may decompose to more stable ions and radicals. In the case of the ion for example, as a result of the exothermic reaction with an available electron, the energy of the neutralization is great enough to break a C-C (or a C-H) bond. The overall process may be represented

schematically:



Among additional possibilities for reactions of the initially produced species are transfer of excitation and ionization between like or unlike molecules, production of radical ions and, to a lesser extent, negative ion formation. Thus, after the formation of the primary ion and excited molecules a variety of secondary processes may occur before bond breakage and subsequent chemical changes result.

The observed chemical changes may therefore be due to a primary positive ion, the free electron, the excited molecule or to ions or radicals which these primary species may produce.

Most evidence at present indicates that these little understood interactions ultimately result in the formation of polymer free radicals, and as a result of the reactions of this macroradical, the chemical changes noted when a polymer is irradiated may include any or all of the following: (1) crosslinking of chains so that higher molecular weight fragments form; (2) chain degradation to low molecular weight fragments; (3) hydrogen formation; and (4) the formation of unsaturated sites in the molecule.

#### Gamma- and X-Rays

For low energy  $\gamma$ - and X-rays (up to about 20-40 Kev) the initial interaction occurs by means of the photoelectric effect, whereby the impinging photon gives up all its energy to the orbital electron it strikes;

this electron may be raised to an excited level or ejected from the atom. The energy of the ejected electron will equal that of the incident photon, less the binding energy of the electron which, for carbon compounds, is a few hundred volts. At higher energies (60 Kev - 25 Mev) Compton scattering becomes important: only a portion of the energy of the incident photon is absorbed in ejecting the electron, and the scattered photons are of lower energy than the initial beam. The interaction can be considered a billiard ball collision between the photon and the electron. The Compton recoil electrons may have energies ranging from 0 to a fraction

$$\frac{2hv}{mc^2 + 2hv}$$

of that of the incident photon, where  $h\nu$  equal the energy of the photon and  $mc^2$  is the rest energy of the electron. The total energy transferred  $dE$ , when  $N$  gamma-photons of energy  $E_0$  pass through a specimen of thickness  $dx$  containing  $n$  electrons per  $cm^3$  is given by the expression

$$dE = NfE_0ndx .$$

In this equation,  $f$  is the fraction of incident energy transferred per recoil electron (the energy absorption coefficient). For 1 Mev  $\gamma$ -bombardment of thin samples, there will be transferred about 3 per cent of the incident beam energy per gram per  $cm^2$  to electrons which can then initiate further ionization and excitation.

For organic polymers, and for about 1 Mev  $\gamma$ -radiation (i.e., from cobalt-60) the density of the Compton electrons is about six per micron of distance traveled in the absorber.

The passage of an X-ray or  $\gamma$ -photon through an organic polymer thus produces one or more fast electrons capable of interacting with the orbital electrons of atoms present in the system in the manner identical for electrons discussed above.

### Neutrons

Neutrons have a mass some 1800 times the mass of the electron and, for neutrons from fission reactions, energies of about 0.01 ev (slow) to 10,000,000 ev (fast). These particles initiate radiation damage mainly by direct attack of the nucleus. When a fast neutron collides with an atom in the polymer, momentum is imparted to the nucleus. The latter recoils, taking with it its electron cloud, and possibly dislodging some of the outermost electrons. Slow neutrons are captured and produce a new nucleus which may be radioactive and decay by  $\beta$ - or  $\gamma$ -emission, or undergo nuclear fission. The effects of neutrons on polymers have not been studied in detail but are probably indirect and depend on the secondary radiations to which they give rise. The damage due to the initial displacement of atoms by the elastic collision is masked by the effects of ionization and excitation.

### $\alpha$ -Particles and Protons

High energy protons and  $\alpha$ -particles interact with organic molecules in the same manner as electrons of the same velocity and charge. The major difference between the heavy particles and the electrons is that the former produce many more ions per unit of path length in the absorber and dissipate their energies much more rapidly.

In the case of polymer irradiations, especially for thin films, no data are available on the spatial distribution of the initially formed



free radicals; it is usually assumed, therefore, that the chemical changes observed occur at random throughout the specimen. The validity of this assumption depends on the ion distribution both along the track of the incident photon and between ions of neighboring tracks.

It might be concluded that the chemical effects of the various radiations discussed are similar since all initially result in the formation of ions and excited molecules capable of decomposing into free radicals. Indeed, for organic systems, indications are that radiation effects depend primarily on the energy absorbed or on the dose rate, but are independent of the nature of the radiation. Whatever the truly initial fragments formed, most of the mechanisms presently proposed to explain radiation effects in polymers successfully postulate the ultimate formation of reactive macroradicals.

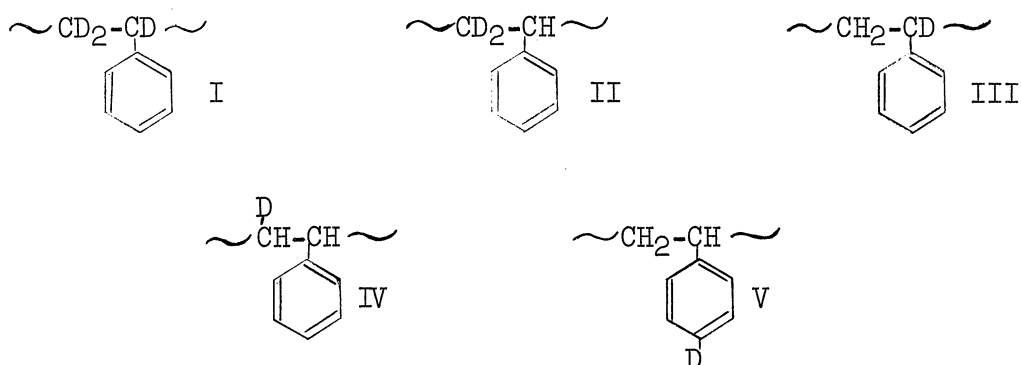
## 2. Radiation Effects in Amorphous Polystyrene

### Crosslinking

Early experiments on the solution properties of in vacuo pile-irradiated bulk polystyrene<sup>(3,4)</sup> revealed that the polymer crosslinks and becomes partially insoluble when irradiated. The solubility in toluene or benzene (both good solvents for this polymer) of irradiated rods was independent of the solvent but decreased rapidly with dose. It appears that in the initial polymer of random molecular weight distribution, crosslinking occurs at random. At high doses, (of the order of 1 pile unit, equivalent to about  $40 \times 10^6 R$ ) only gel is noted, indicating the absence of a simultaneous scission process. The experiments of Schultz and coworkers<sup>(5)</sup> and Feng and Kennedy,<sup>(6)</sup> however, indicate that scission

does occur simultaneously, although the experimental techniques of these workers are suspect. For example, the presence of trace amounts of oxygen would lead to some degradation.

Efforts to determine the site of crosslinking in the backbone are described. Thus, Wall<sup>(7)</sup> irradiated the following deuterated polystyrenes:



and concluded that all of the C-H bonds in the polymer are equally involved in the crosslinking step, i.e., no one bond is preferentially broken. More recent data on the susceptibility to crosslinking of  $\alpha$ -,  $\beta$ - and p-monodeuteropolystyrenes (compounds III, IV and V) by Burlant,<sup>(8)</sup> however, established that only the backbone C-H bonds are involved in the crosslinking step.

It is interesting that the presence of energy absorbing benzene rings in the molecule is manifested in a high degree of radiation stability compared to polyethylene. Thus, the G (crosslink), where G signifies the number of crosslinks formed per 100 ev absorbed, is 0.05 for polystyrene but is about 3 for polyethylene.

#### Gas evolution

The only gas observed when polystyrene is irradiated is hydrogen; the G-value for hydrogen atoms, G(H) has been reported as 0.045<sup>(7)</sup>.

and, more recently as 0.078.<sup>(9)</sup> Mass spectrometric evidence, based on  $\gamma$ -irradiations of deuterated styrenes (IV and V) indicate that backbone C-H bonds are broken<sup>(8)</sup> almost exclusively, i.e., bonds in the benzene ring are unaltered by the radiation.

#### Effect of oxygen

Generally, if oxygen (a diradical) is present during irradiation, a variety of oxidized species are noted, although the precise role of the element in polymer irradiations is not known. For example, in polystyrene and polyacrylonitrile irradiations, its presence results in chain cleavage, which is a changeover in mechanism from the crosslinking observed in vacuo;<sup>(6,10)</sup> nevertheless, it is believed that under these conditions still both crosslinking and scission occur. The scission of polymethyl methacrylate is retarded by oxygen,<sup>(11)</sup> but it is reported that the extent of main chain breakage in polyisobutylene is the same for irradiations in vacuo or in air, although the nature of the breakdown products is influenced by oxygen.<sup>(12)</sup> Polytetrafluorethylene appears to crosslink to a greater extent in vacuo than in air, although in both instances degradation is predominant.<sup>(13)</sup>

#### Mechanical properties

Polystyrene crosslinked with doses as high as  $91 \times 10^8$  R shows<sup>(14,15)</sup> no appreciable change in Young's modulus at 25°; elongation at break, however, decreases slightly and the softening point (normally about 100°) increases somewhat.

These changes in properties are observed at doses great enough so that significant gelation has occurred, i.e., the crosslink density of the system is quite high (1 crosslink per 10-100 monomer units).

Conclusion

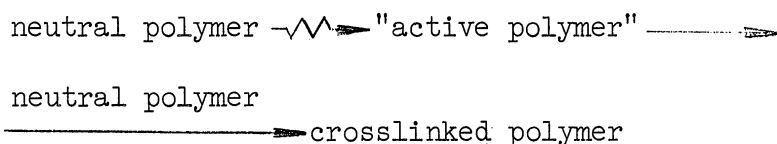
It can be concluded that the predominant effects of high energy radiation on polystyrene are crosslinking and hydrogen gas formation. No data are available on p-substituted polystyrenes.

Mechanism of Crosslinking<sup>(2)</sup>

In polymers which crosslink, the degree of crosslinking is directly proportional to the radiation dose and independent of its intensity, over a  $10^5$  range in intensity. Thus, it is unlikely that two active sites will be formed simultaneously and sufficiently close together to form a crosslink [this would introduce an (intensity)<sup>1/2</sup> dependence].

To date, two general crosslinking modes are considered possible:

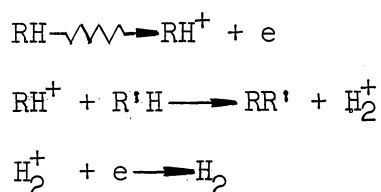
- (1) Each crosslink is the result only of a single ionization or "hit" by the radiation, according to the reaction:



- (2) Each crosslink is the result of two independent radiation "hits" at some distance along the chain, but the ions or radicals subsequently produced from the initially formed ions are mobile enough to move along the polymer chain and from one chain to another until they are close enough so that a crosslink can form.

While crosslinking in specific polymers is described in the literature, sufficient data to establish the mechanism are not yet available; suggested mechanisms for individual polymers are discussed below:

Based on work done on the pile-initiated crosslinking of polyethylene<sup>(16)</sup> and from general considerations of ionic conductivity of irradiated polymers, it is suggested<sup>(17)</sup> that as a result of the primary act, the ionized molecule remaining reacts with a neutral molecule to recapture the electron: This scheme is presented noncommittally as follows, where R = a polyethylene chain.

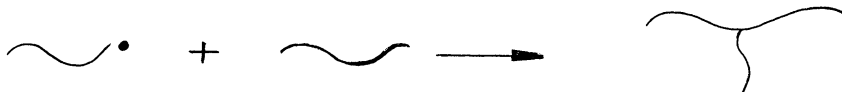


Weiss<sup>(17)</sup> assumes in addition, that the ionic site is mobile, since according to studies of the induced conductivity of irradiated polymers, electrons and ions can move through an irradiated plastic quite readily. At higher temperatures, therefore, it should become easier for crosslinking to occur; for some polymers, e.g., polyethylene this is in fact observed.

Dole<sup>(18,19)</sup> postulated that for the case of irradiated polyethylene, where irradiation results in the rapid disappearance of vinylidene groups ( $\text{RR} = \text{CH}_2$ , present in the original polymer in concentrations of about 4%), the active sites initially formed are mobile and preferentially attack this unsaturated group. Pearson<sup>(20,21,22)</sup> postulates a similar "mobility" theory of crosslinking of polyethylene.

From conductivity measurements on irradiated polymers, some workers<sup>(6,23,24)</sup> feel that the conductivity is due to ion mobility, while others<sup>(25-34)</sup> attribute this phenomenon to the motion of electrons. It is believed that trapped electrons are responsible for the color changes observed in some irradiated polymers.

Crosslinks preceded by main chain fracture are possible, if it is assumed that each fractured end can form a chemical bond to a neighboring polymer.<sup>(35)</sup> This "endlinking" gives rise to branched polymers:



The contribution of "endlinking" to the final crosslinked structure is unknown.

In any mechanism of crosslinking involving random motion of ionic or radical sites along the polymer chain, the presence of "traps" must be considered, for these may alter the frequency of radical or ion transfer from one site to another. Thus, if the time required for an active site to migrate down the chain to a crosslinking position is much greater than the time required for a competing reaction (involving the active site; H atom elimination, for example) the efficiency of the crosslinking step will be low and that of hydrogen evolution will be large. Experiments with polymers (polysiloxanes, for example) containing other chemical compounds as additives present in low concentrations do not permit quantitative evaluation of impurity centers.<sup>(42)</sup>

Marked changes in the susceptibility of a polymer to radiation may be produced in physical admixture of certain additives with the polymer. True radiation protection by small amounts of additives, usually of the order of a few per cent, is probably effected by energy transfer from polymer to additive so that the energy which otherwise would be used for bond breaking is dissipated preferentially by the additive. Aromatic amines, aromatic and aliphatic mercaptans, stearic acid, phenol and anthracene have been employed. Not all of these substances are true

"protectors," i.e., absorb the energy required for bond breaking. Some combine with or furnish H atoms to the initial polymer radicals formed, thereby not permitting the crosslinking reaction to occur. The latter processes<sup>(37,42,45)</sup> are not true "protective" effects.

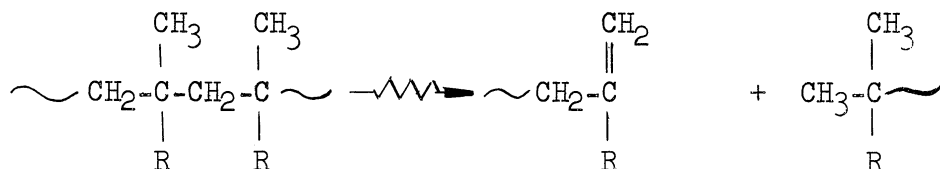
Studies of the viscosity changes and gas yields of  $\gamma$ -irradiated styrene-methyl methacrylate copolymers<sup>(9)</sup> indicate that true internal protection against bond breakage occurs by the energy sinks present - the phenyl rings - but is not transmitted over more than one styrene unit. It may be concluded that the mechanisms for motion of an ionic or radical site along the chain (if these processes occur at all) are not yet understood.

### 3. Steric and Polar Effects

A useful generalization of the effects of radiation on vinyl polymers has been advanced by Wall:<sup>(36)</sup> in the absence of oxygen, polymers that predominantly crosslink when irradiated have higher heats of polymerization than those that degrade. It will be recalled that the heat of polymerization is a measure of the steric hindrance present in the polymer chain: it is low (less than 15 kcal/mole) for strained molecules, and high (greater than 15 kcal/mole) for nonsterically hindered systems. If scission of the main chain into polymer radicals occurs upon irradiation, in a strainless molecule, recombination of the fragments may occur, but disproportionation of the radical sites is likely for a highly strained configuration. Table II summarizes the effects of radiation on some polymers.

Furthermore, it is known that polymers with no  $\alpha$ -hydrogen predominantly degrade when irradiated in vacuo. It has been suggested<sup>(37)</sup>

that when a bulky  $\alpha$ -methyl group is present, scission takes place by a relatively simple rearrangement.



It is of interest that as a result of homolytic C-C or C-H bond cleavage, reactive free radicals may be "frozen" in the rigid polymer matrix yet capable of reacting with those molecules which can diffuse to the radical site; electron spin resonance studies<sup>(38,39)</sup> indicate lifetimes as long as hundreds of hours and spin concentrations of about  $10^{17} - 10^{18}/\text{cc}$ . It has not been established whether the radical sites are at the ends of or along the irradiated chain.

TABLE II

EFFECTS OF IONIZING RADIATION ON POLYMERS<sup>(40)</sup>

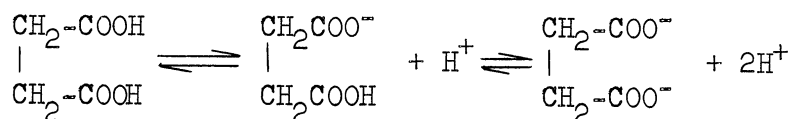
Polymer	H polymerization (Kcal/gmole)	Predominant effect (in vacuo)
Poly- $\alpha$ -methyl styrene	9	degradation
Polymethyl methacrylate	13	degradation
Poly- $\alpha$ -methacrylonitrile	11-13	degradation
Polyisobutylene	13	degradation
Polymethacrylic acid	15.8	degradation
Polystyrene	17	crosslinking
Polybutadiene	17	crosslinking
Polyisoprene	17.9	crosslinking
Polyacrylic acid	18.5	crosslinking
Polymethyl acrylate	18.7	crosslinking
Polypropylene	> 16.5	crosslinking
Polyethylene	22	crosslinking
Polyacrylonitrile	17.3	crosslinking



In 1954, Miller and coworkers<sup>(41)</sup> suggested that in a polymer molecule containing one side group per monomer unit ( $\sim\text{CH}_2-\underset{\text{R}}{\text{CH}}\sim$ ), the removal of an  $\alpha$ -hydrogen atom by radiation leaves a radical molecule which is resonance stabilized with the side group. The liberated hydrogen atom then can abstract a similar  $\alpha$ -hydrogen from a nearby polymer chain giving a second resonance stabilized molecule. The two macroradicals remaining thus are in a favorable position to react. However, in the polymers described,<sup>(41)</sup> it was possible to separate the steric effect from the polar, or resonance effect.

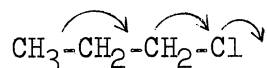
The Hammett Equation:<sup>(46,47)</sup>

In many conventional organic chemical reactions, the formation of the transition state, or of the product, is accompanied by a change in electronic distribution at the reactive site. Such a change in electronic distribution arises from the (1) electrostatic interaction, whereby the change is a result of the external electrostatic field between the reacting molecules and (2) inductive interaction, whereby the electron displacement at a given site in a molecule (arising from the unequal sharing of electrons between unlike atoms) can be transmitted internally through the molecule. The two effects can be illustrated by the following examples:



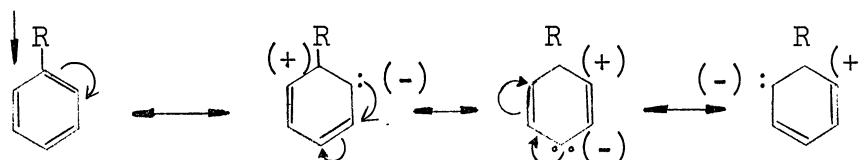
A

1. Electrostatic effect: the work necessary to ionize species A is only the electrostatic work of removing the proton from its position on the carboxyl group to infinity against the attraction of the negative charge.

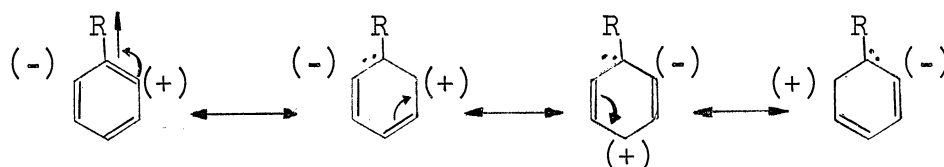


2. Inductive effect: The arrows indicate the direction of electron drift in this molecule; the electrons are concentrated about the -Cl end of the molecule.

A third mode of electron displacement (3) can occur in resonating molecules, i.e., molecules such as benzene,  $\text{C}_6\text{H}_6$ , for which "hybrid" structures of varying electronic configuration may be written. Thus, because of this resonance effect, substituents attached directly to the benzene ring which release electrons into the ring increase the electron density exclusively at the ortho- and para- position, while electron accepting substituents decrease the electron density only at these positions. The following resonance forms for monosubstituted benzenes illustrate these comments:



Effect of electron repelling (electropositive) substituents such as  $-\text{OCH}_3$ ,  $\text{CH}_3$ , on resonance in the benzene ring; the straight arrows indicate the direction of electron drift.



Effect of electron attracting (electronegative) substituents such as  $-\text{NO}_2$ ,  $-\text{CN}$ , on resonance in the benzene ring.

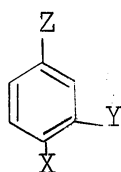
These resonance contributions in benzene nuclei containing substituents of differing electronegativities are independent of the direction of the inductive or electrostatic effects which may be occurring

simultaneously. Furthermore, resonance effects are not transmitted over more than one carbon atom, so that only the  $\alpha$ -carbon atom participates in ring resonance in the case of polystyrenes.

It has been found that the equilibria or rates of several hundred ionic reactions of meta- and para- substituted benzene derivatives, undergoing reaction at a site not directly on the ring (e.g., esterification of p-substituted benzoic acids), can be described by the following empirically derived equation:

$$\log(k/k_0) = \sigma \rho$$

where  $k$  is an equilibrium constant or a rate constant,  $k_0$  is the same for the unsubstituted compound,  $\sigma$  is a constant depending only on the substituent and its position in the ring, and  $\rho$  is a constant depending only on the reaction. This equation holds for reactions which occur in a side chain, Z, attached to the benzene ring containing substituents X and/or Y.



The equation is inapplicable to ortho-substituted derivatives because little understood steric factors are of great significance in the reactions of ortho-derivatives.

The values of  $\sigma$  and  $\rho$  have been determined by taking  $\rho$  for the ionization of benzoic acids in water at 25° equal to 1. A positive  $\sigma$  indicates that the substituent increases the ionization constant; a positive  $\rho$  means that the particular reaction being studied responds to electron displacements in the same manner as does the ionization of benzoic

acids, i.e., the reaction is accelerated by electron-attracting groups and retarded by electron releasing groups. Attempts to explain the Hammett equation in terms of molecular orbital theory are described in the literature.<sup>(47)</sup> Table III summarizes established average values for the substituents employed in the present study.

TABLE III  
VALUES OF  $\sigma$  FOR SUBSTITUENTS IN THE PARA POSITION

Substituent	$\sigma$
CH <sub>3</sub> O	-0.268
CH <sub>3</sub>	-0.170
H	0.00
Cl	0.227
Br	0.232
CN	0.628
NO <sub>2</sub>	0.778

The Hammett constants cannot be used to relate substitution reactions which occur directly at a carbon atom in the benzene ring, e.g., nitration of p-substituted benzenes. In reactions of this kind, resonance interaction between the p-substituent and the active site in the molecule can occur, and the prevailing view is that this resonance interaction (which depends on the electronic environment about the attacking fragment) will vary widely from reaction to reaction so that the electronic contribution of the substituent could not possibly be represented by a single constant.

To reflect the role of polar substituents in the latter cases in terms of the resonance effect of these substituents, a new set of  $\sigma$

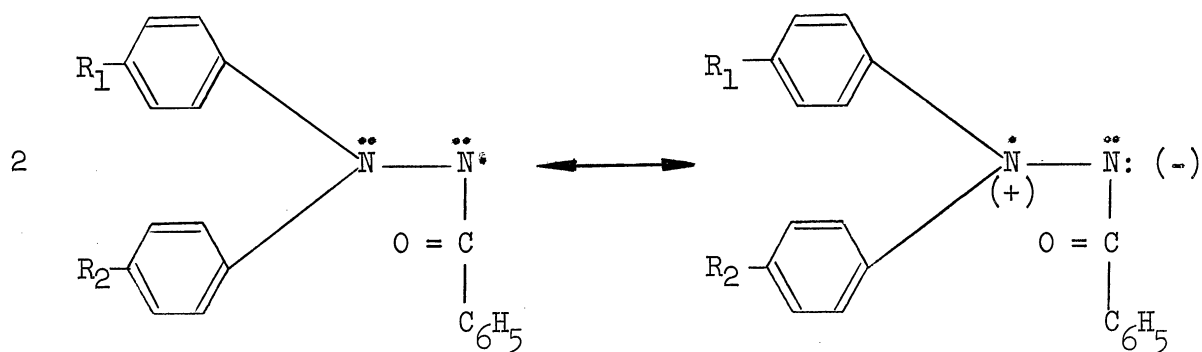
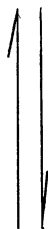
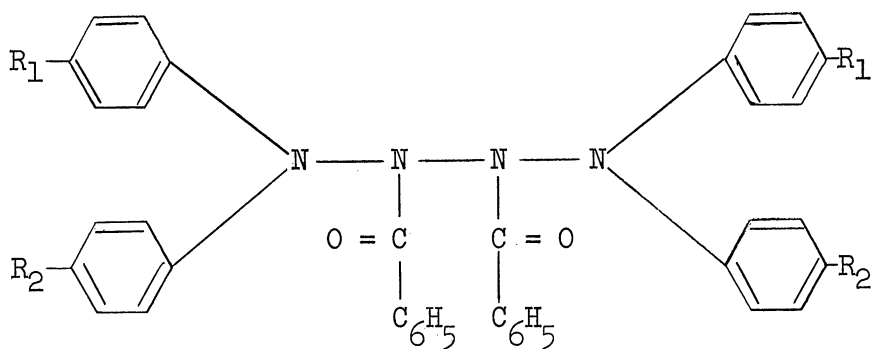
constants ( $\sigma^+$ ) for these systems is suggested.<sup>(50)</sup>  $\sigma^+$  -Values also are empirically determined (Table IV) in a manner identical to the scheme for determining the original  $\sigma$ -values, but based on the solvolysis of p-substituted phenyldimethyl carbonyl chlorides.

TABLE IV<sup>(50)</sup>

REVISED  $\sigma$  CONSTANTS ( $\sigma^+$ ) TO TAKE INTO ACCOUNT RESONANCE EFFECTS

OCH <sub>3</sub>	-.764
CH <sub>3</sub>	-.306
Cl	.227
Br	.232
NO <sub>2</sub>	.778

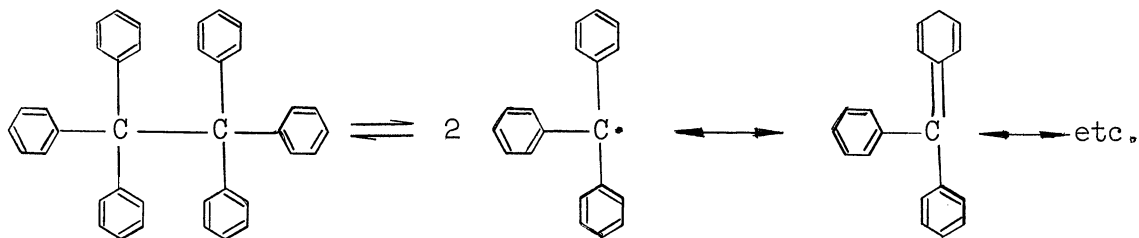
Within the last few years, the equation has been applied with a fair degree of success to explain the kinetics of a few free radical reactions: polar effects have been observed<sup>(51)</sup> in the attack upon C-H bonds of bromine atoms, chlorine atoms, peroxyradicals and N-succinimidyl radicals. For example, the equilibrium dissociation constants for substituted tetrazines have been determined.<sup>(58)</sup> In this system, it is postulated that there is no resonance interaction of the odd electron on the nitrogen with the para-substituent; it appears only that the substituents exert their normal inductive effects through the rings, and that electron donating substituent stabilize the radical by reducing the partial positive charge carried by the  $\alpha$ -nitrogen. If the odd electron interacts with the para-substituent, as, for example occurs in the dissociation of the



where  $R_1$  and  $R_2 = \text{CH}_3, \text{H}, \text{Br}, \text{NO}_2$ .

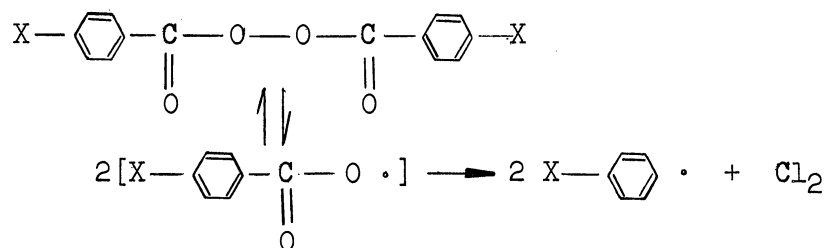
### Dissociation of Substituted Tetrazines

hexaphenylethanes, (67)



the Hammett relation does not hold because both positive and negative  $\sigma$  substituents stabilize the odd electron.

Studies also are reported (49) of the effects of substituents on one or both benzene rings of benzoyl peroxide on the rate of its spontaneous decomposition:

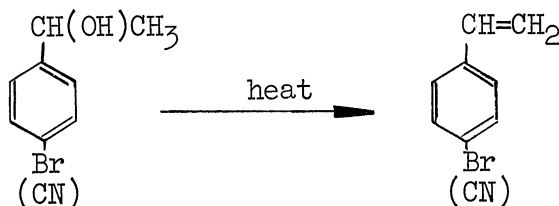


It was found that electropositive substituents on one or both of the phenyl rings increase the rate of the unimolecular decomposition, whereas electronegative groups retard the reaction. Again, the resonance-stability of the oxygenated radicals formed after cleavage is not an important factor in determining the rates: it seems that in this case, the two benzoate groups in the starting peroxide are dipoles attached in such a way as to repel each other. Cleavage into free radicals occurs because of this electrostatic repulsion. Electropositive groups in the para-position increase the repulsion and facilitate bond breakage; electronegative groups decrease the negative charge on the central oxygen atom, reduce the electrostatic repulsion and lower the decomposition rate.

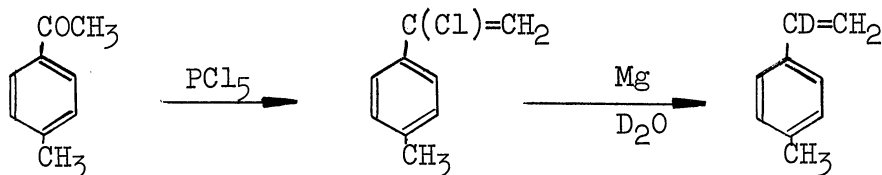
## II. EXPERIMENTAL PROCEDURES

### A. Preparation of Vinyl Monomers. p-Bromostyrene and p-Cyanostyrene

These monomers were prepared according to a described procedure,<sup>(52)</sup> by pyrolysis of the corresponding p-bromo- or p-cyanophenylmethyl carbinol:



$\alpha$ -d<sub>1</sub>-p-methyl Styrene. This monomer was prepared in 40 per cent yield according to the following scheme:



Thus, dry Mg turnings (23.4 g; 0.97 moles) were placed in a 1 liter flask equipped with a water-cooled condenser, dropping funnel and magnetic stirrer. To the flask was added a crystal of iodine and the apparatus thoroughly flamed out in a dry nitrogen atmosphere. When the flask cooled to room temperature, enough tetrahydrofuran was added to cover the Mg, and addition of a solution of 65.7g. (0.44 moles) of  $\alpha$ -chloro-p-methylstyrene (prepared as described in the literature<sup>(53)</sup>) in dry tetrahydrofuran was begun. The reaction started after about 1/4 of the solution was added; addition was rapid enough to ensure mild refluxing. Refluxing was continued for one hour after addition was complete, then cooled to room temperature. Hydrolysis of the Grignard was effected by the dropwise addition of 100 ml of D<sub>2</sub>O (obtained in 99.9 per cent purity from the Stuart Oxygen Company, California) followed by 25 ml of H<sub>2</sub>O.



Several hundred ml of ethyl ether then was added to the mixture, and the organic layer removed. The residue was further extracted several times with ether and benzene and the combined solution washed with saturated NaCl solution then dried over  $\text{CaCl}_2$ . Distillation afforded a pale green liquid previously unreported, boiling at 66-68° at 18mm, in 40 per cent yield. Its refractive index,  $n_{20}^D = 1.5423$  Analysis: Calcd. for  $\text{C}_9\text{H}_9\text{D}$ : C, 90.7; H, 9.3. Found C, 90.2; H, 8.5. From mass spectrometric data of similarly prepared deuterated ethyl benzenes, and from the disappearance of the 6.2 and 6.3  $\mu$  peak in the infrared absorption spectrum of the product, accompanied by the appearance of a peak at 4.6  $\mu$ , it is estimated that the deuterium content is between 96-99 per cent of the theoretical amount.

Other Monomers. The remaining p-substituted styrenes were commercially available, well characterized materials.

#### B. Preparation of Polymers

All monomers were redistilled or recrystallized several times, degassed in vacuo, and polymerized thermally to low conversions (to minimize chain branching). The polymers were dissolved several times in suitable solvents; benzene was satisfactory for all the polymers except poly-p-nitrostyrene, for which N,N-dimethyl formamide was employed. The polymer was isolated by precipitation from solution with methyl alcohol, then dried in vacuo.

A few polymers were prepared in the presence of oxygen to determine the effect of the O atom incorporated in the polymer chain on the radiation chemistry of the system.

Second order transition temperatures of the polymers were estimated from sticking points determined on a standard melting-point hot stage. All were in the range of  $80^{\circ}$ - $120^{\circ}$ . The reported value for polystyrene is about in this range.

### C. Sample Irradiations

#### Radiation Source

The cobalt-60 irradiation facility at the Phoenix Memorial Laboratory of the University of Michigan was used for the sample irradiations. Cobalt-60 emits 2  $\gamma$ -rays of energies of 1.17 and 1.33 Mev.

This facility consists of a 5,000 curie cobalt-60 source ( $\pm$  300 curies) which is arranged in a squirrel cage configuration, and kept in a well of water when not in use. The sample tubes were placed at calibrated dose rate-marked positions on the floor, before the cobalt-60 is raised.

The source was calibrated using the Fricke  $\text{Fe}^{++}$  -  $\text{Fe}^{+++}$  dosimetry technique, as described by Weiss.<sup>(54)</sup> It has a maximum dose rate of about  $1.0 \times 10^6$  R per hour in the inside well of the cylindrical configuration. The error in the calibration of the source is less than  $\pm$  10 per cent. The facility has been in constant use since 1955, and repeated calibrations have been performed.

About 0.1g.  $\pm$  0.0001g. of the solid polymers were degassed in 18 x 100-200 mm pyrex ampules for several hours at  $80^{\circ}$ , in vacuo. The ampules then were necked down so that the upper few mm. had an outside diameter of about 2 mm, then sealed in vacuo. Figure 1 is a photograph of the sealing assembly. Mass spectrometric examination of the gases in the ampule before irradiation indicated the absence of oxygen.

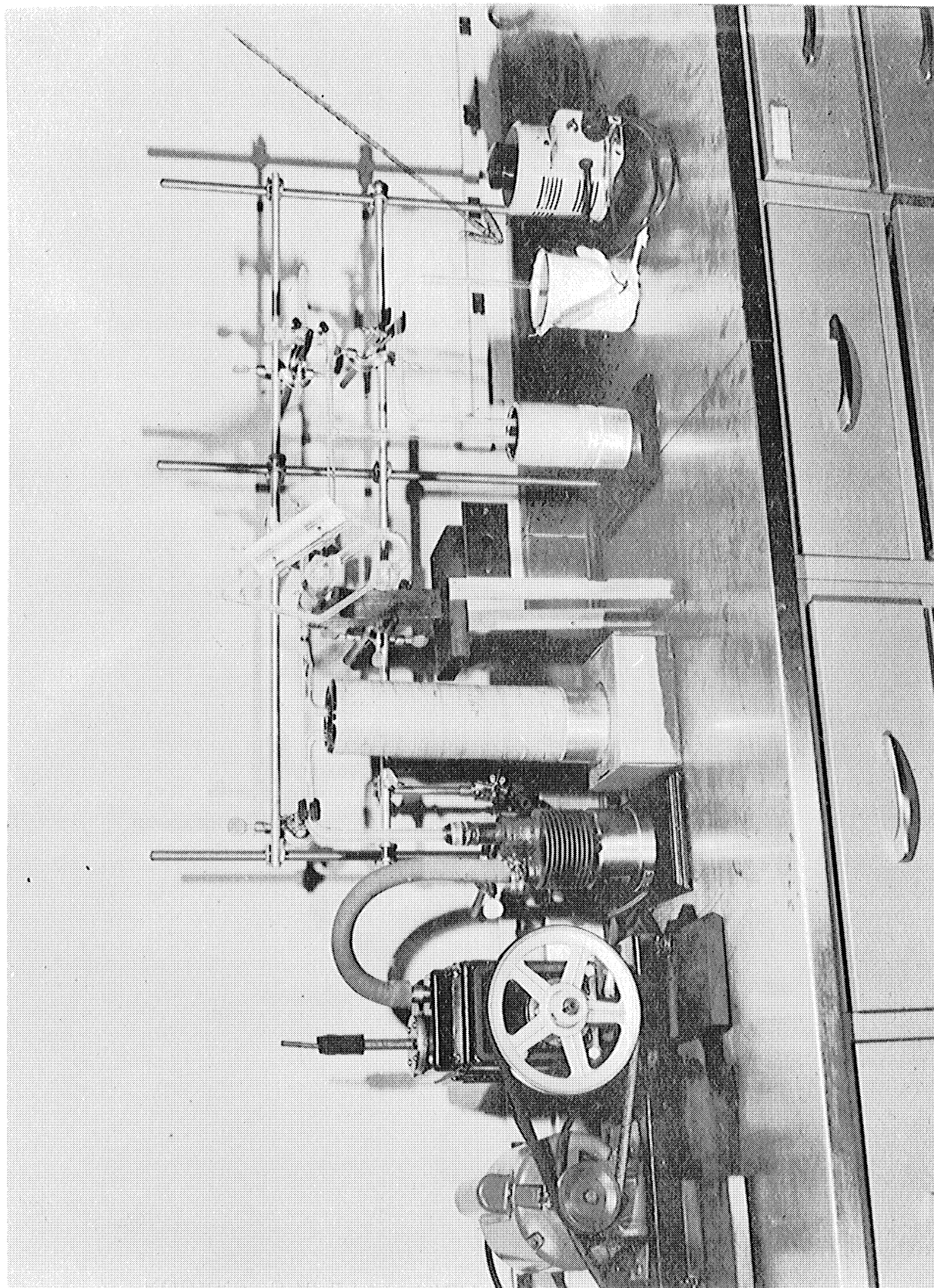


Figure 1. Sealing assembly for the  $\gamma$ -irradiation of the p-substituted polystyrenes; the sample tube is indicated by the arrow.

The samples were irradiated at a dose rate of  $2.3 \times 10^5$  R per hour, which was obtained at a distance of about 13.5 cm from the center of the source, with the sample centered about the middle plane of the source. Total doses ranging from  $2.3 \times 10^5$  to  $10^7$  R were employed for most of the experiments.

For irradiations at lower temperatures the samples were set in Dewar flasks with walls about 0.5 cm thick, and then positioned at the distance mentioned above. The samples were placed against the wall of the flask, so that the cooling materials would not reduce the dose received by them.

Irradiations at room temperature were performed by simply setting the samples at this distance for the time necessary to obtain the desired dose.

For temperatures higher than room temperature, an electrically controlled, magnetically stirred oil bath was used, controllable from outside the radiation cave. Temperatures were measured by using a thermocouple, and were constant to  $\pm 1^\circ\text{C}$ .

#### D. Gas Evolution Measurements

A few days after irradiation, the ampules were sealed into a Consolidated Model No. 21-103 mass spectrometer.

The conventional inlet system of the instrument was modified to permit analysis of about  $10^{-10}$  moles of gas by eliminating the usual 3 liter inlet volume; the gas was introduced directly into the filament chamber.

The ampules were sealed to the instrument by means of a Teflon gasketed compression seal, then opened to the inlet system by means of a

stainless steel bellows sealed breakoff<sup>(69)</sup> (Figure 2). For the present study, this was a convenient technique.

The actual quantities measured were in the region of  $10^{-9}$  moles of gas. Absolute quantities are believed to be within 10 per cent of the true values; relative concentrations within a few per cent. More than 90 per cent of the gases in each tube were accounted for.

Errors and manipulative difficulties in the mass spectrometric analyses due to adsorption of water vapor on the sample were minimized by flushing the system only with argon between analyses. In this manner, mass analyses of the ampules could be effected rapidly, accurately and with good precision.

Separate experiments with irradiated polystyrene established the fact that even at  $-200^{\circ}\text{C}$ , hydrogen quantitatively diffuses out from the sample essentially instantly and that errors due to diffusion characteristics of the system hydrogen-polymer can be ignored for the present study.

With the exception of poly-p-methoxystyrene, the only significant gas produced was hydrogen. From the latter polymer, in addition to  $\text{H}_2$ ,  $\text{CH}_4$  was a major product. Trace quantities of halogenated solvents, which were employed in isolating and purifying the materials, as well as  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  were detected in many of the ampules. The contributions to the  $\text{H}_2$  peak by the hydrogen-containing gases were taken into account in calculating the gas yields, but these gases were considered impurities and their contributions to the mechanism neglected in the present work.

$G(\text{H}_2)$  was calculated by assuming that polymer given a dose of  $0.93 \times 10^6$  R absorbs  $5.8 \times 10^{19}$  ev/gram, i.e., that the electron density

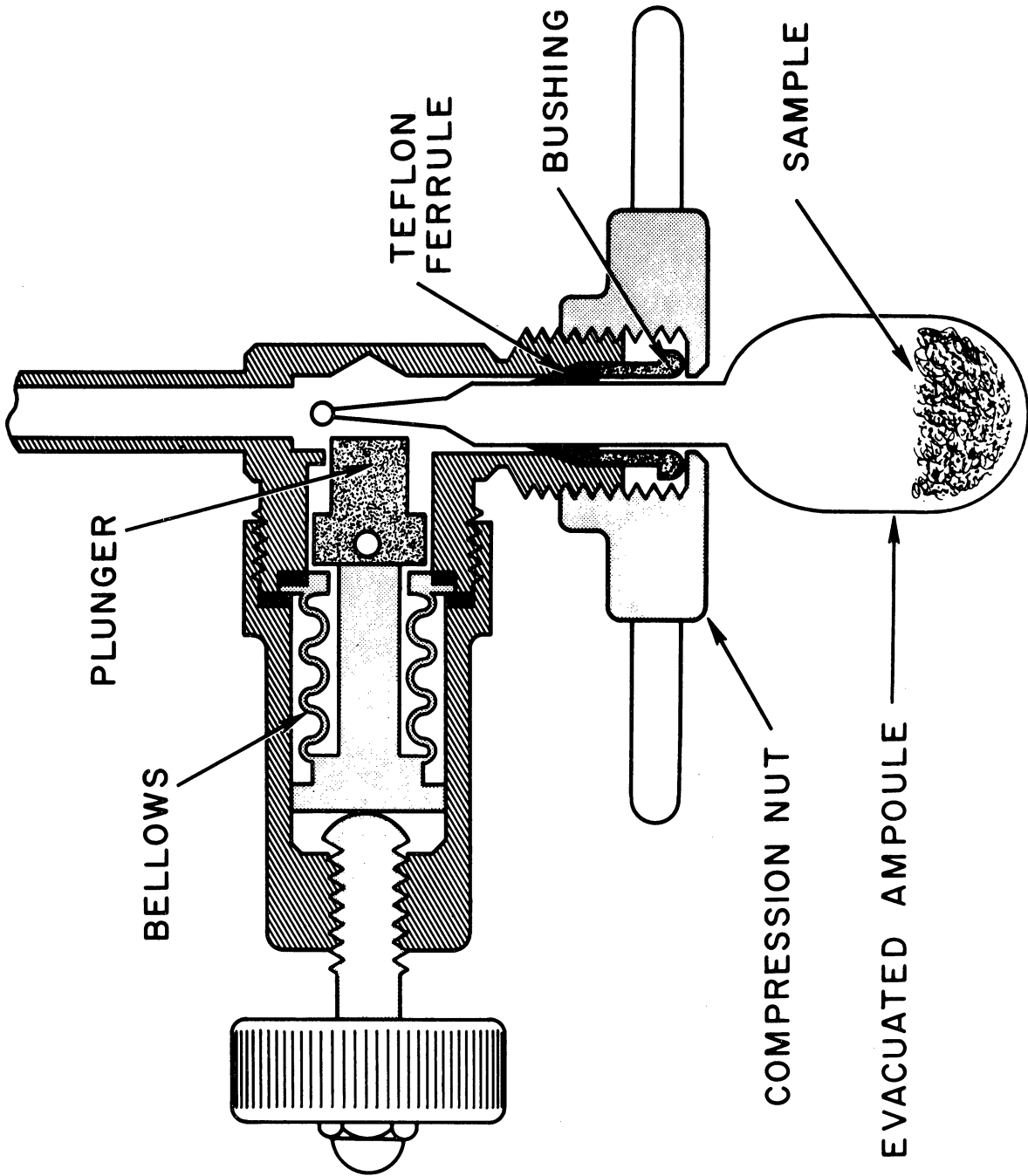


Figure 2. Teflon gasketed compression seal used to seal ampoules to mass spectrometer.

of the polymer is about equal to that of water. Thus,

$$G(\text{H}_2) = 100 \times \frac{\text{Avogadro's No.} \times g}{5.8 \times 10^{19} \times W \times d}$$

where

g = the gram-moles of  $\text{H}_2$  liberated from the sample;

W = the weight in grams of the polymer sample, and

d = dose in  $\text{R} \times 10^{-6}$ .

$G(\text{CH}_4)$  was calculated similarly. Errors in  $G(\text{gas})$  are estimated to be  $\pm 10$ - $20$  per cent of the true values, and reproducible to within  $\pm 5$  per cent.

#### E. Molecular Weight Data and $G(\text{Crosslink})$

A conventional Ubbelohde dilution viscometer was employed to measure the viscosity changes of the irradiated polymers, according to known procedures. The temperature during these measurements did not vary more than  $\pm 0.1^\circ\text{C}$ ; flow times were measured to  $\pm 0.1$  sec, and were reproducible to  $\pm 0.3$  sec.

Exactly 5.00 cc of the polymer solution of known concentration (about 1 per cent) was pipetted into the viscometer and its flow time determined. Flow times at successively dilute concentrations were measured by adding known volumes of solvent directly to the viscometer. Complete mixing was obtained by gentle air bubbling. In this manner  $\eta_{\text{sp}}/c$  at four concentrations ( $c$  in gm of polymer/100 cc of solution) was determined, where

$$\eta_{\text{sp}} = \frac{\eta_{\text{s}} - \eta_{\text{o}}}{\eta_{\text{o}}} .$$

In the latter expression,  $\eta_s$  and  $\eta_o$  are the flow times (in seconds) of the polymer solution and the pure solvent, respectively. Intrinsic viscosities,  $[\eta]$ , in dl/gm were determined graphically by plotting  $\eta_{sp}/c$  vs  $c$  and extrapolating to infinite dilution to eliminate the interaction effects between adjacent polymer molecules.

With the exception of the p-NO<sub>2</sub> and p-CN polymers, the relation between  $[\eta]$  and number-average molecular weight is reported for the polymers employed in the present study. Table V summarizes the appropriate data.

For the former systems, therefore,  $\gamma$ -ray initiated fractional changes in molecular weights were calculated by assuming that in the equation

$$[\eta] = KM^\alpha$$

$\alpha$  is 0.7. The error introduced by this assumption is probably small:

- (a) it has been shown by Flory<sup>(57)</sup> that  $\alpha$  varies between 0.5 and 1.0 and (b)  $\alpha$  is about this value for the polymers used in the present work.

Thus, let

$M_o$  = molecular weight of non-irradiated polymer

$M_1$  = molecular weight of irradiated polymer

$[\eta]_o$  = intrinsic viscosity of non-irradiated polymer

$[\eta]_1$  = intrinsic viscosity of irradiated polymer

Then:

$$[\eta]_o = KM_o^\alpha \quad \text{or} \quad M_o = ([\eta]_o/K)^{1/\alpha}$$

$$[\eta]_1 = KM_1^\alpha \quad \text{or} \quad M_1 = ([\eta]_1/K)^{1/\alpha}$$



$$\begin{aligned} \text{and the fractional change in } M &= \Delta M = \frac{M_1 - M_0}{M_0} \\ &= \frac{[\eta]_1^{1/\alpha} - [\eta]_0^{1/\alpha}}{[\eta]_0^{1/\alpha}} \end{aligned}$$

A 4 per cent change in the measured  $[\eta]$  results in a 6 per cent change in  $\Delta M$ . Note that  $K$ , unknown for the p-nitro- and p-cyanopolymers, does not appear in the final expression for  $\Delta M$ .

$G(\text{crosslinks})$  for a particular system is the number of crosslinks formed per 100 ev absorbed; it was calculated from the change in the number average molecular weight of the polymer upon irradiation. Thus:

$$\text{Let the no. of chains present} = \frac{\text{total no. of monomer units in the sample}}{\text{no. average DP of the chain}}$$

and let  $2Y = (\text{no. of polymer chains present before irradiation}) - (\text{no. of chains present after irradiation})$

$$\text{then } G(\text{crosslink}) = \frac{100 Y}{(58 \times 10^{18} \times \text{dose in R})}$$

The calculations of  $G(\text{crosslink})$  from gel data are described in section III-D. Both methods yield  $G(\text{crosslink})$  estimated to be within  $\pm 20$  per cent of the actual values, and reproducible to  $\pm 10$  per cent. The largest source of error in this measurement is the determination of molecular weights in the 300,000 range.

While  $G(\text{crosslink})$  is independent of chain length, both radiation initiated changes in molecular weight and doses required for incipient gelation depend on the length of the polymer chain.

For some calculations, the weight-average molecular weight is a more meaningful parameter. In the absence of such experimental data, it

is assumed that the molecular weight distribution for the various polystyrenes is a random one, so that the weight-average molecular weight = twice the number-average molecular weight.<sup>(60)</sup> This relationship has been verified by other workers for the polystyrene irradiated in this study. Inasmuch as the p-substituted polystyrenes were of the same molecular weight (when prepared under identical conditions) as the unsubstituted polymer, this assumption appears to be a valid one.

Although no molecular weight data are available on the p-NO<sub>2</sub> and p-CN polymers, it will be seen that this information in no way alters the conclusions of the experiments, because of the remarkable stability toward radiation-crosslinking of the two materials. From measurements of  $[\eta]$ , it is estimated that molecular weights of the latter are in the same range as those of the other polymers.

TABLE V  
INTRINSIC VISCOSITY--NUMBER AVERAGE MOLECULAR  
WEIGHT DATA FOR SOME POLYSTYRENES<sup>a</sup>

Polymer	Constants in the Equation $[\eta] = KM^\alpha$		Approx. molecular weight of polymer used in this work
	K	$\alpha$	
Poly-p-Chlorostyrene <sup>(55)</sup>	$2.8 \times 10^{-5}$	0.77	418,000
Poly-p-Bromostyrene <sup>(56)</sup>	$1.6 \times 10^{-3}$	0.5	400,000
Poly-p-Methylstyrene <sup>(59)</sup>			370,000 <sup>b</sup>
Polystyrene <sup>(57)</sup>	$1.0 \times 10^{-4}$	0.74	250,000
Poly-p-Methoxystyrene <sup>(58)</sup>	$2.4 \times 10^{-4}$	0.66	330,000

(a) All in benzene, at 20-25° except the methoxy derivative, data for which was reported for toluene solutions; for this study the  $[\eta]$ 's from benzene solutions were recalculated for toluene solutions from experimental data detd. in this lab. all data on unfractionated polymers, except for the p-bromo-polymer.

(b) Calculated from the equation reported<sup>(59)</sup> for 2 per cent solutions:  $\eta_{sp} = 1.8 \times 10^{-4} C(M)$  where C = molar conc. of monomer units giving a specific viscosity of  $\eta_{sp}$ .

### Dose Required for Incipient Gelation

The dose for incipient gelation, i.e., the dose, D, just required to produce an infinitesimally small quantity of gel is taken as that dose at which the molecular weight increases exponentially; D is determined graphically.

### Branching in a Polymer

The following empirical equation has been derived by Huggins:  
$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c$$
 where  $k'$ , called the Huggins constant, is considered an indication of the degree of branching in the system and the other symbols have their usual significance. It is seen that from this equation,  $k'$  can be determined from the slope of the  $\eta_{sp}/c$  vs.  $c$  curves and  $[\eta]$ . As the degree of branching in a polymer increases,  $k'$  increases. While quantitative data on the length or distribution of the pendant chains cannot be obtained from  $k'$ , relative "extents of branching" can be estimated.

### Spectra

Infrared absorption spectra were determined on a Perkin Infracord on liquid films in the case of monomers, and from films of the polymers deposited from benzene or N,N-dimethyl formamide solution. Ultra-violet absorption spectra of the polymer films were determined on a Beckman model DK recording spectrophotometer.

### III. RESULTS AND DISCUSSION

Hydrogen yields and the susceptibility to crosslinking (the latter obtained from molecular weight data both in the pre-gel region and in the region around the gel point) were determined for the p-substituted polystyrenes listed on Table I.

Figure 3 shows that the p-substituents do not introduce steric hindrance in the molecule; it may be assumed, therefore, that in fact, the only change resulting from this substituent is a polar one.

#### A. Preliminary Experiments

##### 1. Effect of Impurities

Table VI summarizes comparative data for several polymers prepared both in vacuo, and in the presence of air. For the latter polymers, it may be assumed that O atoms are incorporated in the chain or attached to it; the incorporation of O in polymers in this fashion is well known.

TABLE VI  
EFFECT OF OXYGEN ATOMS ON THE  
RADIATION CHEMISTRY OF POLYSTYRENES<sup>a</sup>

-X	Temp. °C	G(H <sub>2</sub> ) x 10 <sup>2</sup>		Fractional Change in M.W.	
		Pure	Oxygenated	Pure	Oxygenated
OCH <sub>3</sub>	-195	3.04	2.74	0.004	.13
NO <sub>2</sub>	-195	0.32	0.40	0.02	-.24
NO <sub>2</sub>	-80	0.60	0.48		
NO <sub>2</sub>	25	2.61	1.46	-.06	-.03

(a) Dose rate,  $2.3 \times 10^5$  R/hr; total dose,  $4.6 \times 10^5$  R; all samples irradiated in vacuo.

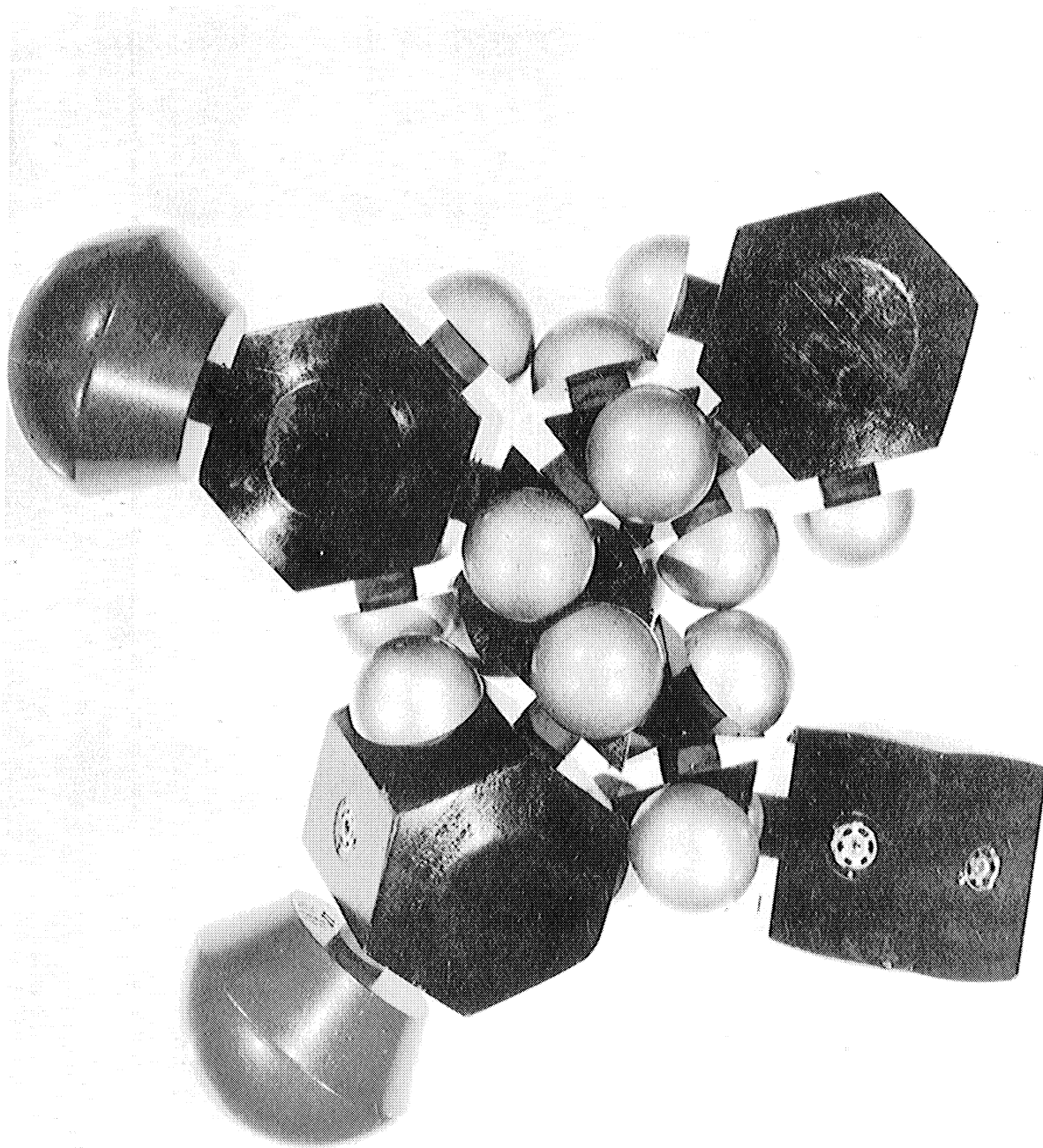


Figure 3. Molecular model of poly-p-bromostyrene indicating the absence of steric hindrance in the backbone by the p-substituent. For clarity, some atoms have been removed from the benzene ring.

It is apparent that the role of impurity centers in polymer irradiations is not to be discounted. Thus, for the case of the p-nitro polystyrene complete changeover in mechanism from crosslinking to degradation is observed when oxygen atoms are in the molecule. If oxygen is incorporated in the polymer as peroxide links,  $\sim\text{O}-\text{O}\sim$ , (in accord with known data for the polystyrene system, for example) some of the results are not unexpected because such links are weaker than C-C and C-H bonds and perhaps are preferentially cleaved when irradiated. Average bond energies are summarized in Table VII.

TABLE VII  
SOME AVERAGE BOND ENERGIES (ev/bond)

H-H	4.5	C-Br	2.8	C-Br(aromatic; estimated, 4)
C-C	3.5	C-I	2.5	
C-H	4.3	O-O	1.5	C-Cl(aromatic; estimated, 5)
C-C	6.1	C-O	3.3	
C-Cl	3.4	C-N	2.9	

Surprisingly, while the crosslinking process is sensitive to oxygen, the  $G(\text{H}_2)$  values are rather insensitive. On this basis alone, it appears that the mobility of the active sites along the chain (see page 13) is not a major factor in hydrogen formation, and that this gas is the result of a direct bond breaking step.

All subsequent experiments were with polymers prepared in vacuo from thoroughly degassed monomers.

## 2. Dose Rate Dependence

Further preliminary experiments with polystyrene and poly-p-nitrostyrene confirmed the conclusions in the literature that the

crosslinking and hydrogen formation processes are independent of the dose rate. The range briefly examined in the present study was  $0.46 \times 10^5$  to  $2.3 \times 10^5$  R/hr.

B. Hydrogen Yields

Except for poly-p-methoxystyrene,  $H_2$  was the only significant gas detected when the p-substituted polymers were  $\gamma$ -irradiated at the single dose of  $4.5 \times 10^6$  rad; irradiation of the p-OCH<sub>3</sub> polymer produced CH<sub>4</sub> in addition to H<sub>2</sub>. Table VIII summarizes the raw data for these systems and Table IX lists the corresponding  $G(H_2)$  and  $G(CH_4)$  values.

TABLE VIII

MASS SPECTROMETRIC ANALYSIS OF GASES PRODUCED FROM  
THE  $\gamma$ -IRRADIATION OF p-SUBSTITUTED POLYSTYRENES<sup>a</sup>

p-Substituent	Moles H <sub>2</sub> , x 10 <sup>9</sup>				Moles CH <sub>4</sub> , x 10 <sup>9</sup>			
	Temp. °C				Temp. °C			
	-195	-80	25	63-69	-195	-80	25	63-69
-OCH <sub>3</sub>	19.4	15.2	27.1	18.4	15.4	11.3	36.8	46.2
-CH <sub>3</sub>	19.4	19.7	33.3	21.0				
-H	11.1	15.0	19.3	18.5				
-Br	0.8	1.8	3.3	5.1				
-Cl	0.8	5.0	5.1	7.9				
-CN	3.6	3.5	5.2	4.6				
-NO <sub>2</sub>	1.8	3.3	12.3	11.9				

(a) Sample weights of about 0.10 g; total dose,  $4.6 \times 10^6$  R.

TABLE IX

G(H<sub>2</sub>) AND G(CH<sub>4</sub>) VALUES FOR THE  $\gamma$ -IRRADIATION  
OF p-SUBSTITUTED POLYSTYRENES<sup>a</sup>

p-Substituent	G(H <sub>2</sub> )				G(CH <sub>4</sub> )			
	Temp. °C				Temp. °C			
	-195	-80	25	63-69	-195	-80	25	63-69
-OCH <sub>3</sub>	0.036	0.032	0.046	0.038	0.028	0.023	0.064	0.099
-CH <sub>3</sub>	0.038	0.043	0.055	0.047				
-H	0.023	0.031	0.039	0.040				
-Br	0.0035	0.0054	0.017	0.020				
-Cl	0.0016	0.010	0.017	0.017				
-CN	0.0073	0.0076	0.014	0.010				
-NO <sub>2</sub>	0.0032	0.0048	0.026	0.023				

(a) total dose,  $4.6 \times 10^6$  R.

The purpose of the present study is the determination of the overall relative susceptibility to cleavage of C-H bonds in the backbone of the p-substituted polymers. The polarity of the p-substituent will be manifested in a change in the electron density of the  $\alpha$ -carbon atom of the polymer, as well as at the ortho C-H bonds of the ring. Recent studies<sup>(8)</sup> with both ring and backbone deuterated polystyrenes (discussed above) indicate that the backbone, almost exclusively, undergoes C-H bond breakage. Thus, it was reasonable to assume that in the p-substituted polymers studied in the work, the polarity of the substituent might indeed be reflected in the susceptibility to bond breakage only of the  $\alpha$ -C-H bond of the backbone. In the present study, experimental evidence for this specificity is indicated by the absence of halogens, halides, nitrogen oxides and nitriles in the effluent gases of the irradiated



polymers, and from the fact that  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  are not detected from the p- $\text{CH}_3$  and p- $\text{OCH}_3$  polymers, respectively. It is concluded safely, therefore, that the p-substituted polymers do not undergo decomposition at the bond between the substituent and the ring.

On the other hand examination of the structure of the p- $\text{CH}_3$  and p- $\text{OCH}_3$  polymers suggest that the C-H bonds in these substituents are as susceptible to breakage as the backbone C-H bonds. Thus, the chemical and steric environment about both sites is approximately the same. For this study, therefore, it was essential to ascertain the contribution to the  $\text{H}_2$  produced of both backbone and substituent for polymers containing C-H bonds in the substituent.

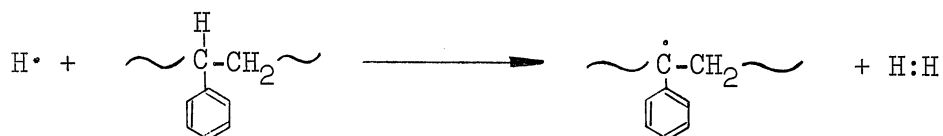
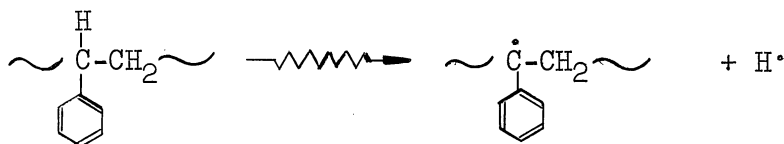
The correction was based on gas yield from the  $\gamma$ -irradiation of 0.100 gm. samples of the following selectively deuterated polymers. (Table X):

TABLE X  
 $\gamma$ -IRRADIATION OF DEUTERATED POLYSTYRENES<sup>a</sup>

Polymer	Yield of HD, moles x $10^9$	Yield of $\text{H}_2$ , moles x $10^9$	Total yield of H, g atoms x $10^9$	[D]/[H]	Isotope Effect
Polystyrene		23.9	47.8		
Poly- $\alpha$ - $\text{d}_1$ - styrene	1.6	17.1	35.8	0.045	4.38
Poly-p- methyl styrene		33.3	66.6		
Poly- $\alpha$ - $\text{d}_1$ - p-methyl styrene	2.3	21.0	44.3	0.052	4.78

(a) Total dose,  $9.3 \times 10^6$  R

The p-CH<sub>3</sub>-polymer liberates about 40 per cent more H<sub>2</sub> than polystyrene. From the results of the α-d<sub>1</sub>-polymers, it is clear that about 44 per cent more D is liberated from the p-CH<sub>3</sub> polymer. From data published<sup>(8)</sup> on the mechanism of H<sub>2</sub> formation in γ-irradiated polystyrene, it was shown that this gas is formed in part, by a radical abstraction process and that the α-carbon atom is preferentially attacked by the H· initially liberated:



On the basis of the latter conclusion, the excess D in the p-CH<sub>3</sub> polymer arises from the increase in the number of H atoms available for abstraction; furthermore, H abstraction by D is more likely in the polymer which has more C-H bonds available. If the [D]/[H] ratio for the various deuterated polymers is examined, it is seen that within experimental error, the values are about the same for the two polymers.

It is concluded from these results that much of the H<sub>2</sub> detected from the γ-irradiation of the p-CH<sub>3</sub> polystyrene arises from the decomposition of the p-substituent and that the backbone is not activated by the substituent.

For this study it is further assumed that the -CH<sub>3</sub> group in p-OCH<sub>3</sub> polystyrene is as susceptible to attack as the -CH<sub>3</sub> group in p-CH<sub>3</sub> polystyrene. Sufficient data are not available to assign quantitative significance to the relative susceptibility toward cleavage of the

bonds in these polymers. Qualitatively, however, on the basis of these assumptions and from the  $G(\text{H}_2)$  values of Table IX, it appears that the backbones of all the p-substituted polymers liberate less  $\text{H}_2$  than polystyrene.

### 1. Temperature Effects

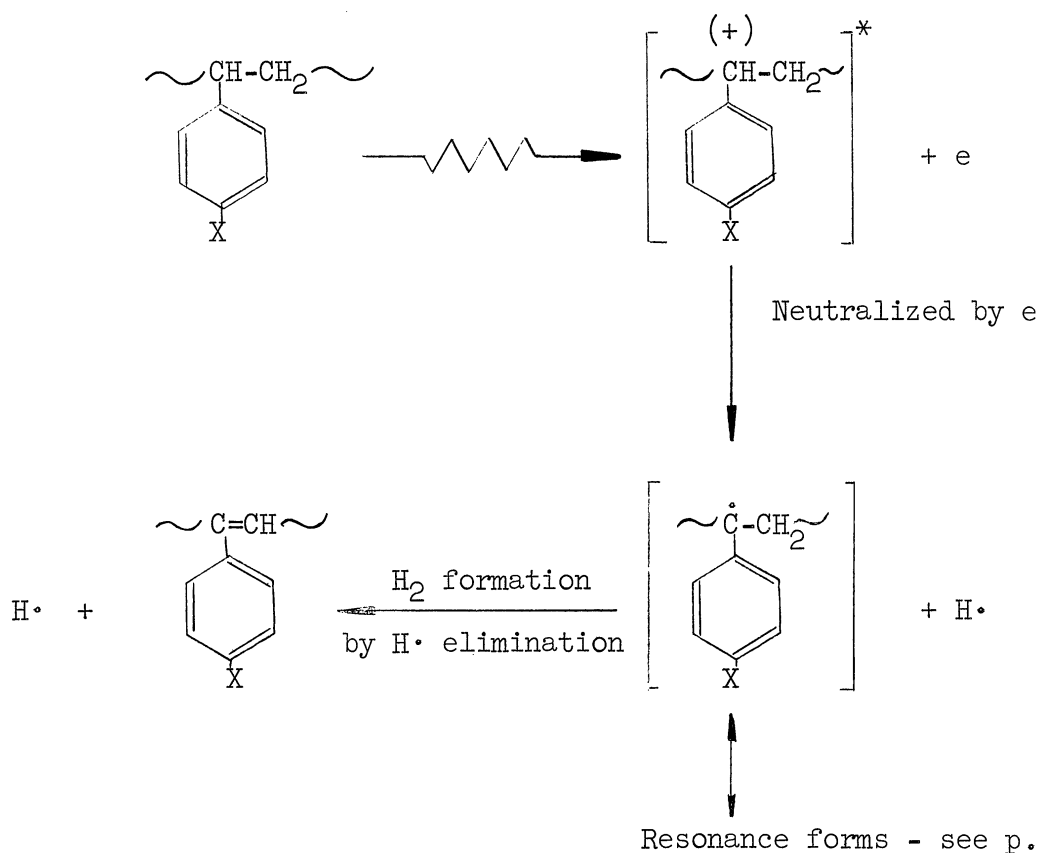
On the basis of experiments only at three temperatures, while the overall apparent activation energy for  $\text{H}_2$  formation [obtained from plots of  $\log(\text{rate of formation of } \text{H}_2) \text{ vs. } 1/T_{\text{abs}}$ ] is very low for all the samples, little fundamental significance attaches to this observation inasmuch as other rate factors (gas diffusion through the solid, for example) are implicit in the data.  $\gamma$ -Initiated chemical changes in polymers would be expected to have low apparent activation energies, and this, in fact, is reported for some systems.<sup>(9)</sup>

### 2. Mechanism of Gas Formation

#### a. Hydrogen

It was discussed earlier, that it is not possible to present a precise mechanism for the formation of hydrogen molecules when polymers are  $\gamma$ -irradiated because the nature of the initial interaction between  $\gamma$ -photon and polymer molecule is not understood. Nevertheless, the experimental results indicate the significant effect on the  $\text{H}_2$  yields of p-substituents of differing electronegativities. These data, together with data of other workers<sup>(62)</sup> on radical processes in the gas phase, suggest that resonance stabilization of the polymer radical formed early in the irradiation is responsible, in part, for  $\text{H}_2$  production according to the

following scheme:



Such a mode of H<sub>2</sub> formation (and of radical stabilization by elimination of an adjacent H atom) is statistically favored because of the availability of 4 C-H bonds capable of eliminating H atoms. This mechanism of H<sub>2</sub> production is well established for gaseous radicals;<sup>(62)</sup> the activation energy for this step in the gas phase is estimated at 40-50 kcal/mole.<sup>(65,66)</sup>

The detection of olefins via infrared absorption spectra is not possible because the concentration of this species is low; no change was noted in the spectra of the irradiated polymers. From ultraviolet absorption spectra of thin films, (Figure 4), it is seen that increased absorption occurs in the irradiated materials. Unfortunately, the interfering

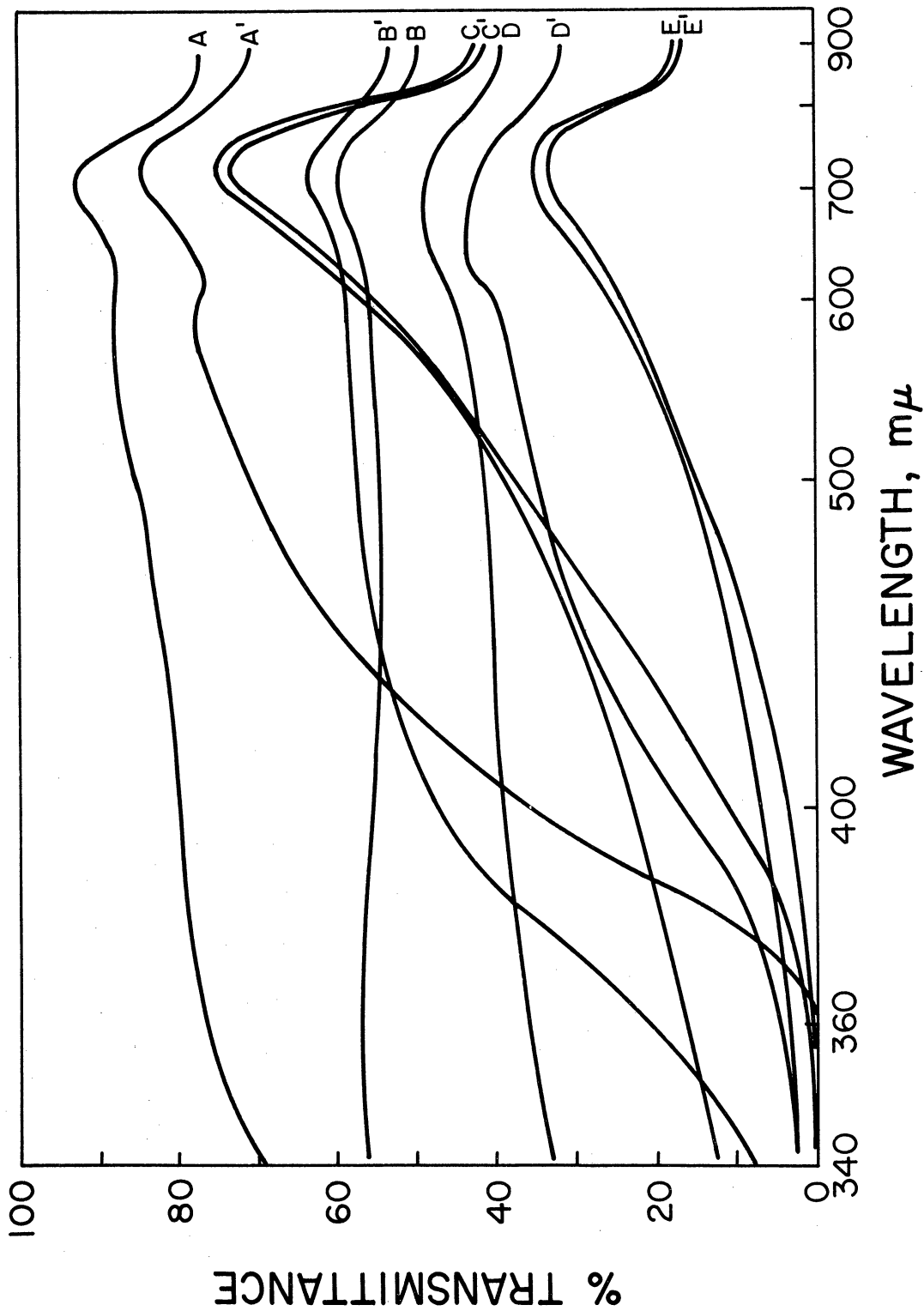
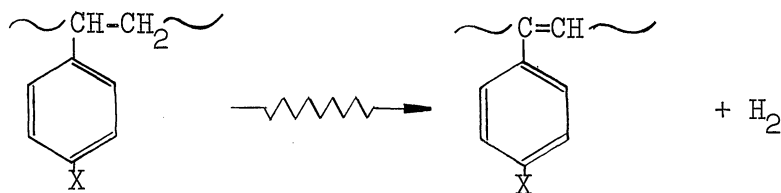


Figure 4. Ultraviolet absorption spectra of unirradiated and irradiated (prime letters) polymer films: A, B, C, D and E represent the p-methyl-, unsubstituted, p-chloro-, p-methoxy- and p-bromopolymers, respectively.

strong absorptions by the phenyl groups, present in all the polymers, precludes quantitative analyses of these phenomena. It was not possible to prepare films of the p-NO<sub>2</sub> polymer.

While some of the free H<sup>•</sup> produced may combine to give H<sub>2</sub>, (activation energy, 0), experiment with deuterated polymers indicate that a likely mechanism for H<sub>2</sub> formation, at least when the concentration of H<sup>•</sup> is extremely low, is a radical abstraction step. The energy of activation for such a step is about 9 kcal/mole.<sup>(64)</sup>

The liberation of H<sub>2</sub> by a molecular process is also possible; and, in fact, is known for some low molecular weight systems.<sup>(63)</sup> For the polystyrenes, this mode may be indicated as follows:

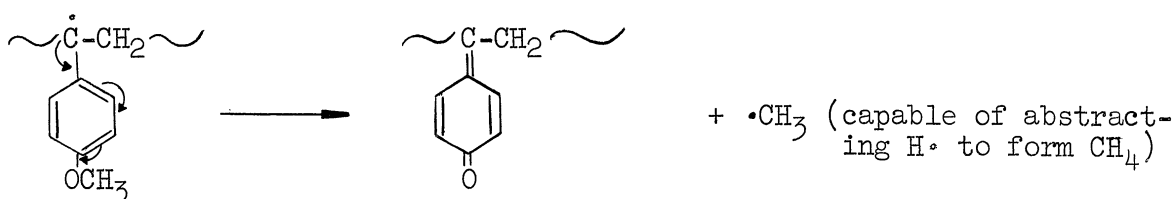


In the gas phase, for low molecular weight hydrocarbons, the energy of activation for this process is 50-60 kcal/mole.<sup>(63)</sup>

Thus, at the lower temperatures, the predominant processes would be expected to be H atom abstraction and recombination, but molecular elimination and H atom elimination would be likely as the temperature is raised. In the absence of sufficient thermodynamic and kinetic data, the relative importance of these steps cannot be ascertained at present; nor can the contribution to the H<sub>2</sub> yield of ionic processes if these occur, be evaluated.

b. Methane

The formation of  $\text{CH}_4$  from the poly-p-methoxystyrene, a result of cleavage of the  $-\text{OCH}_3$  group cannot be explained in terms of bond strengths alone, for the strength of the C-O bond is about that of the C-C bond. It is suggested that the driving force of the reaction leading to  $\text{CH}_4$  is the stability of the quinoid product, formed according to the following scheme:



The lack of correlation of  $G(\text{gas})$  values with the Hammett  $\sigma\text{-}\rho$  scheme is offered as further, indirect proof of the importance of resonance stabilization of radical species in these processes.

C. Crosslinking1. Resonance Effects

All the p-substituted polystyrenes either crosslinked when irradiated, or, within experimental error, exhibited no change in molecular weight in the dose range and temperature range ( $-200^\circ$  to  $25^\circ$ ) studied. Figures 5 to 18 summarize the raw data relating the measured intrinsic viscosity  $[\eta]$  with the total dose and temperature of irradiation, at a constant dose rate of  $2.3 \times 10^5$  R/hr. Table XI summarizes the dependence of  $G(\text{cross-link})$  on the electronegativity of the substituent, and on the total dose.

Excluding the p-halopolymers for the moment, it is superficially apparent that while electron withdrawing groups lower the susceptibility

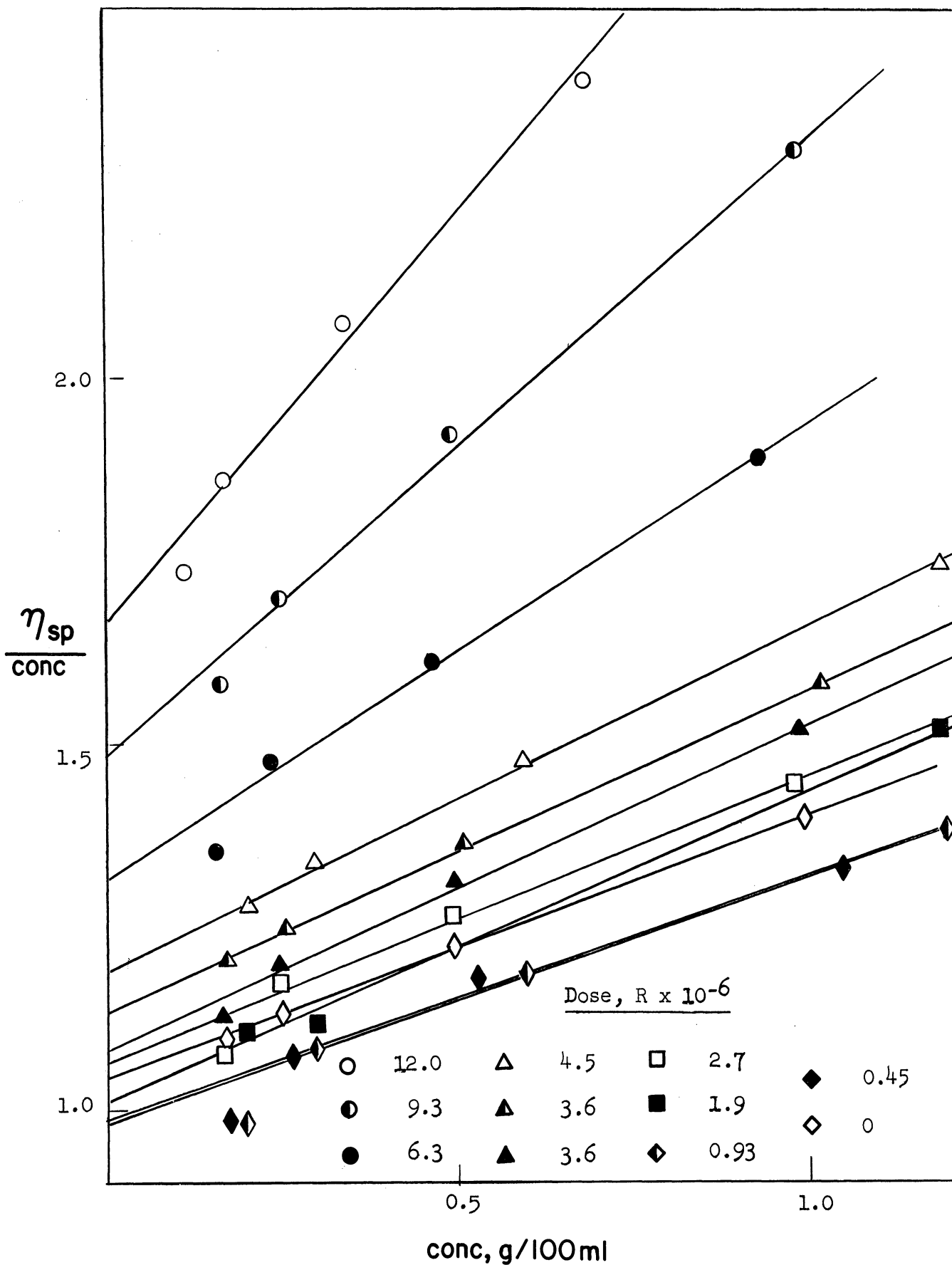


Figure 5. Dependence of  $[\eta]$  on total dose for  $\gamma$ -irradiated poly-p-methoxystyrene, at 25°C.



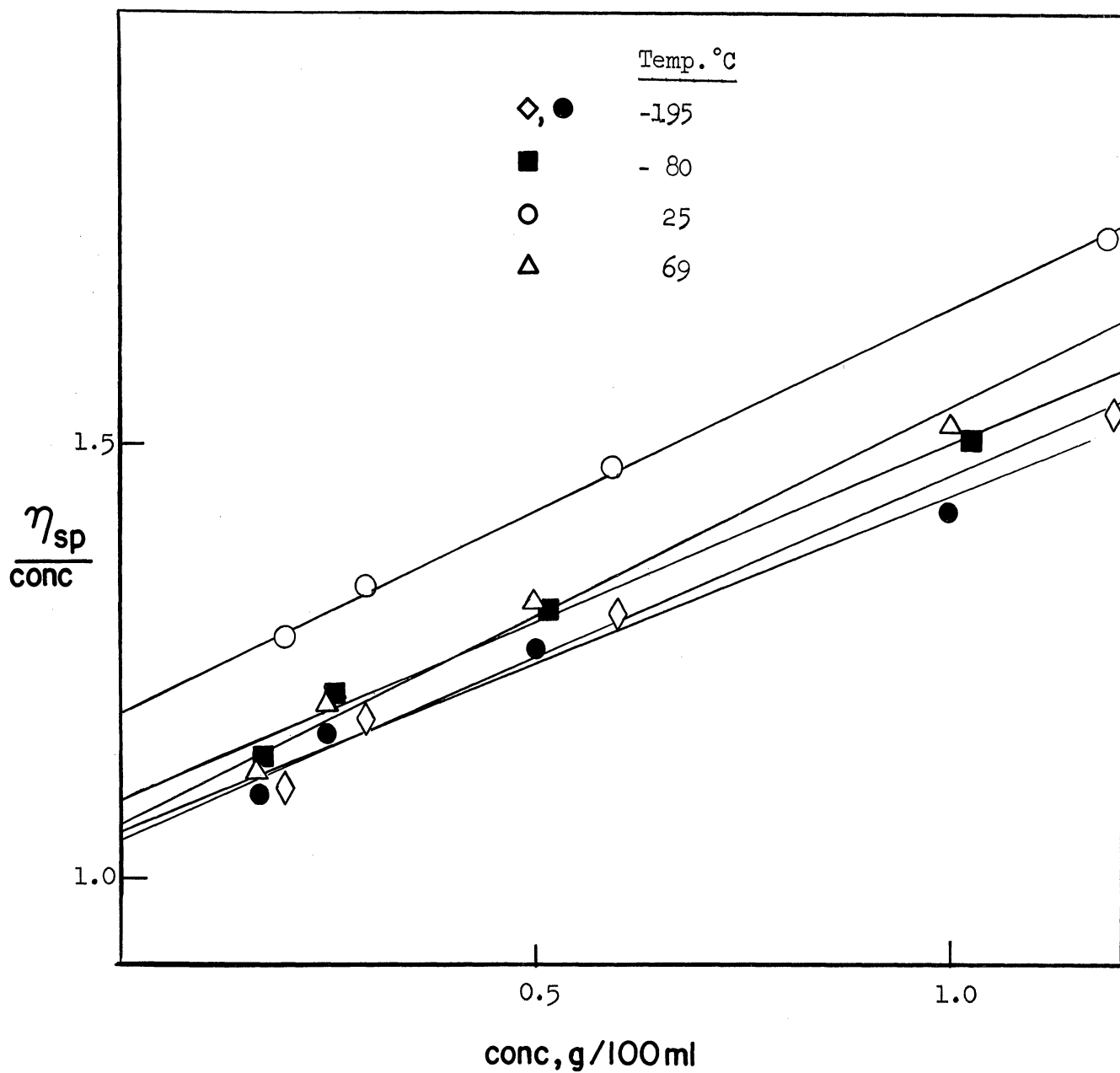


Figure 6. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-methoxystyrene on the temperature of the irradiation, at a total dose of  $4.5 \times 10^6$  R.

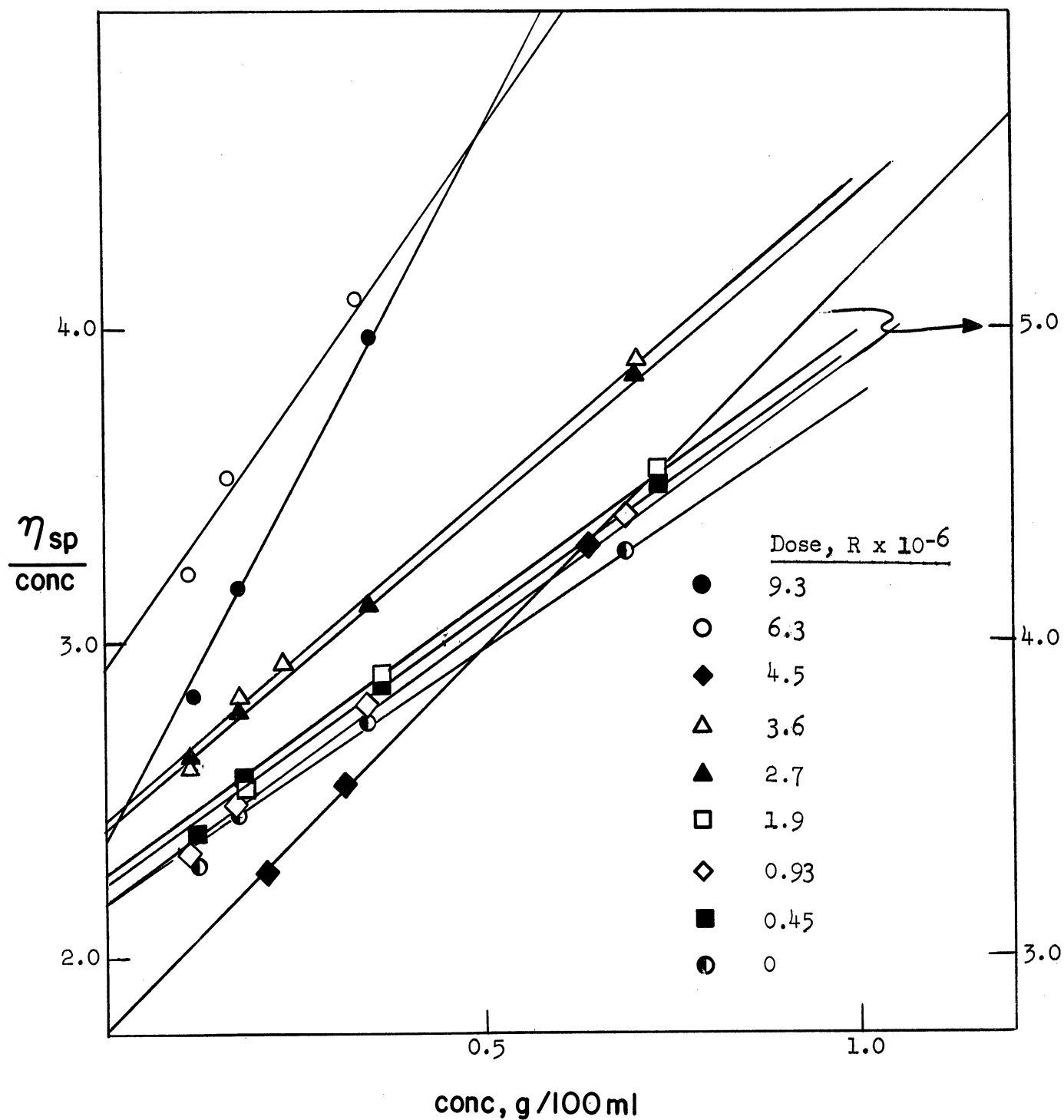


Figure 7. Dependence of  $[\eta]$  on total dose for  $\gamma$ -irradiated poly-p-methylstyrene, at 25°C.

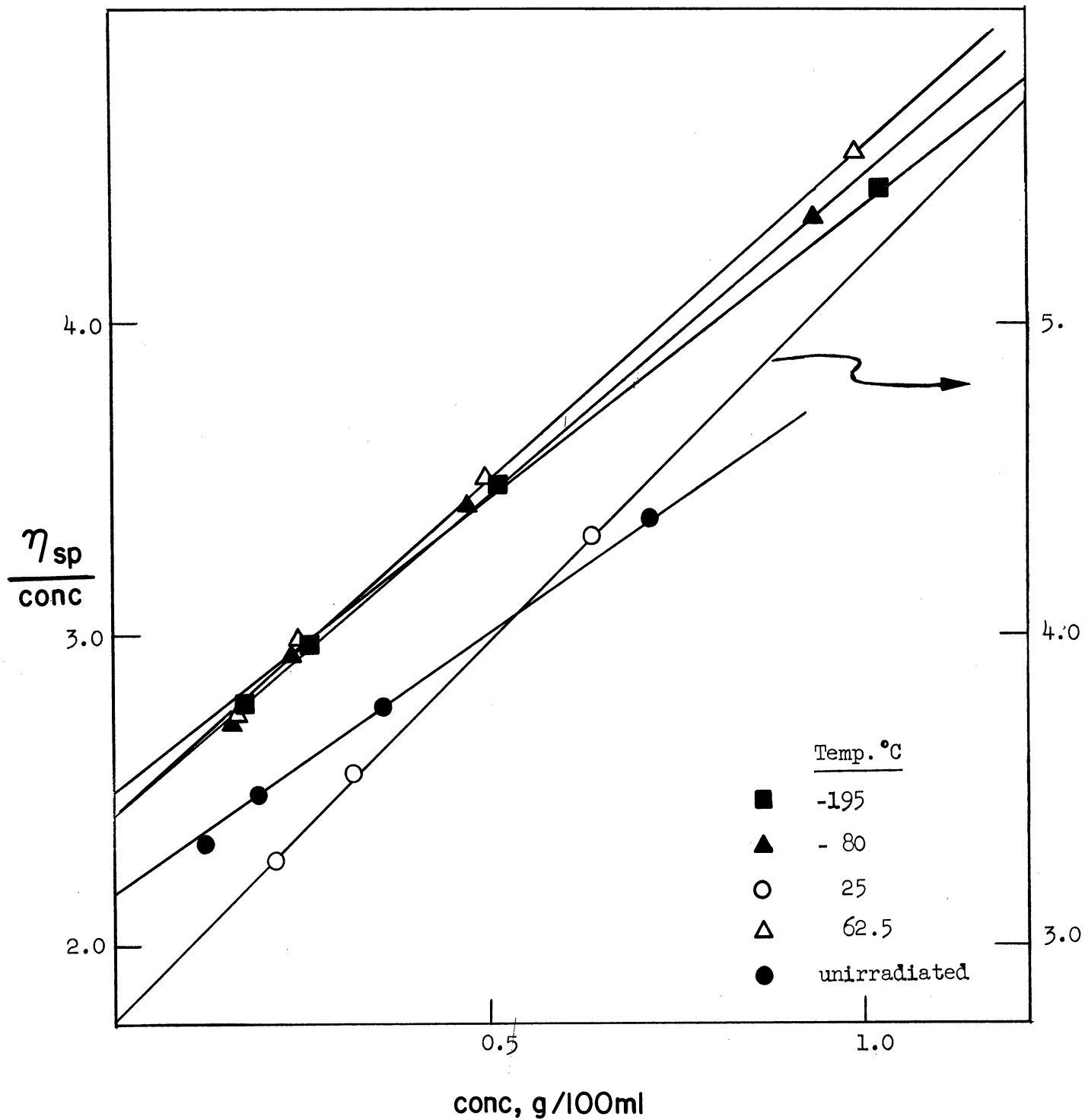


Figure 8. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-methylstyrene on the temperature of the irradiation, at a total dose of  $4.5 \times 10^6$  R.

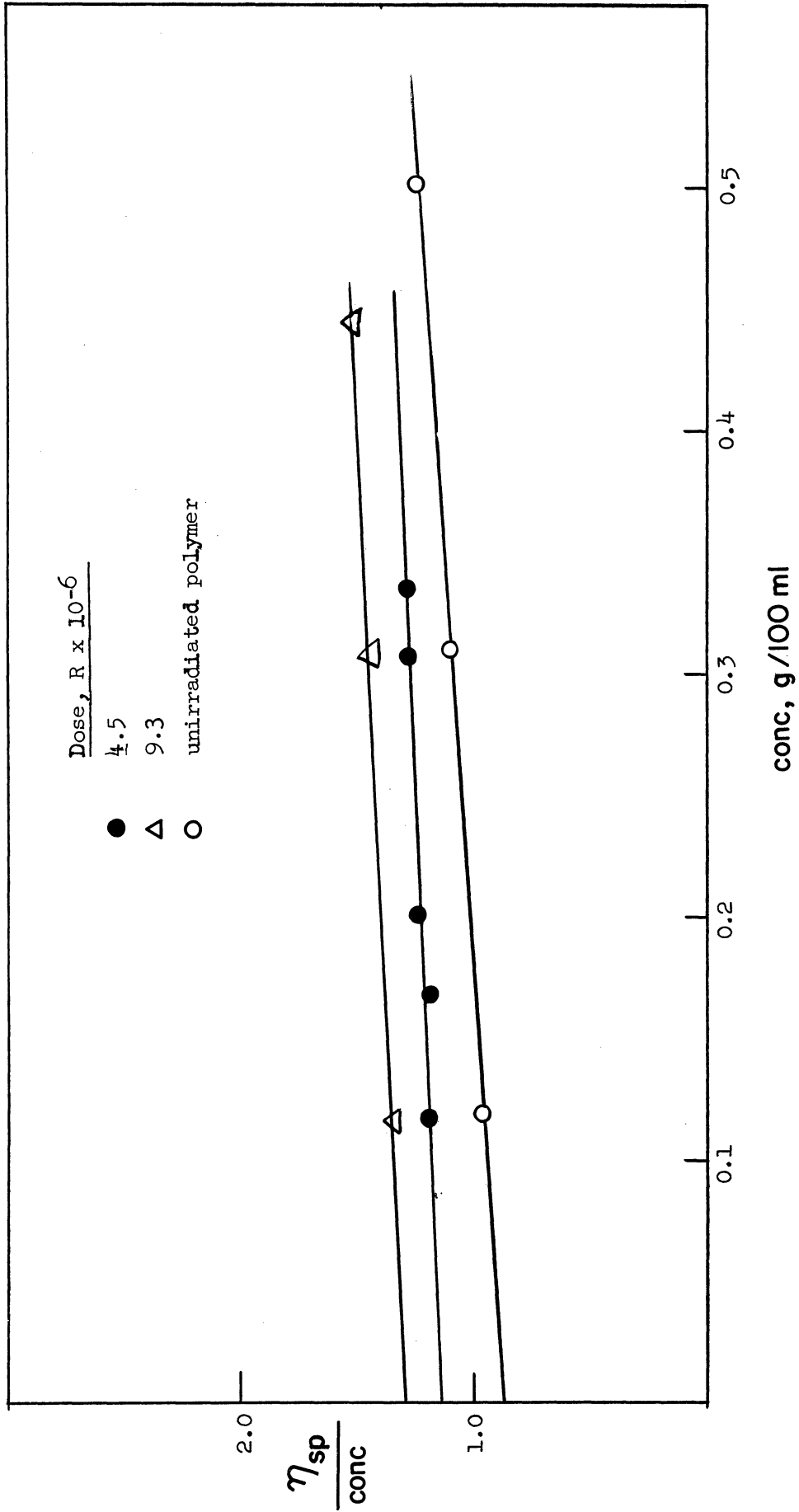


Figure 9. Dependence of  $[\eta]$  of  $\gamma$ -irradiated polystyrene on the total dose ( $4.5 \times 10^6 R$ , upper curve), at  $25^\circ C$ .

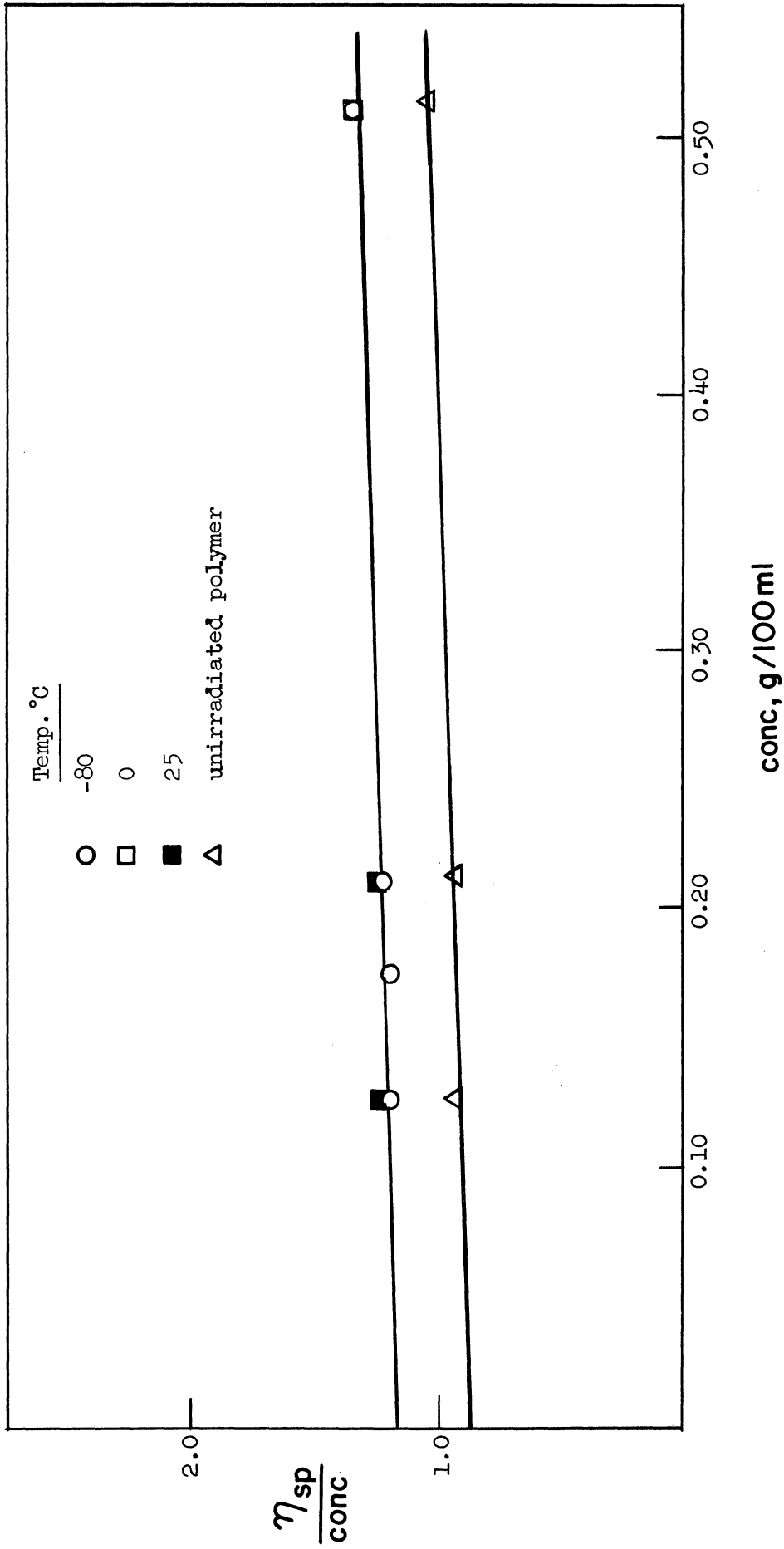


Figure 10. Dependence of  $[\eta]$  of  $\gamma$ -irradiated polystyrene on the temperature of the irradiation, at a total dose of  $4.5 \times 10^6$  R.

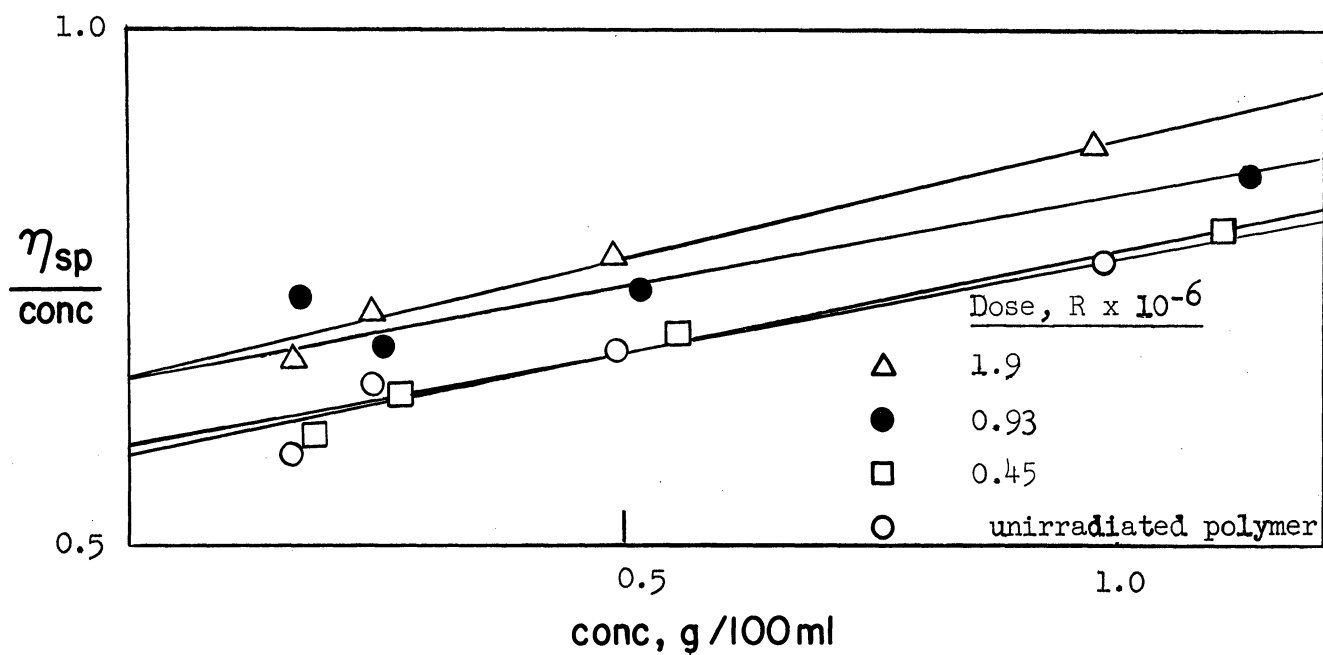


Figure 11. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-chlorostyrene on the total dose, at 25°C.

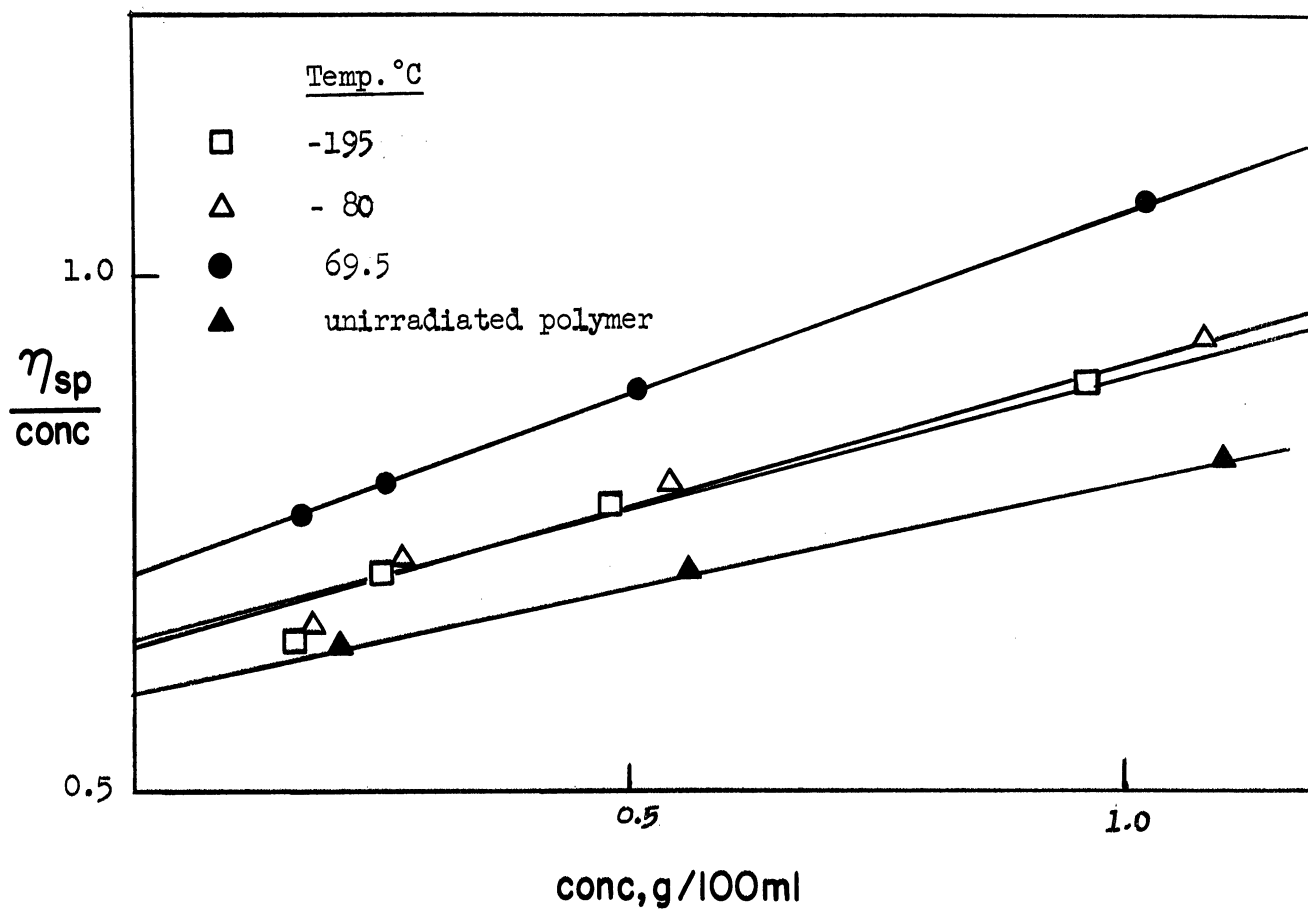


Figure 12. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-chlorostyrene on the temperature of the irradiation, at a total dose of  $2.8 \times 10^6$  R.

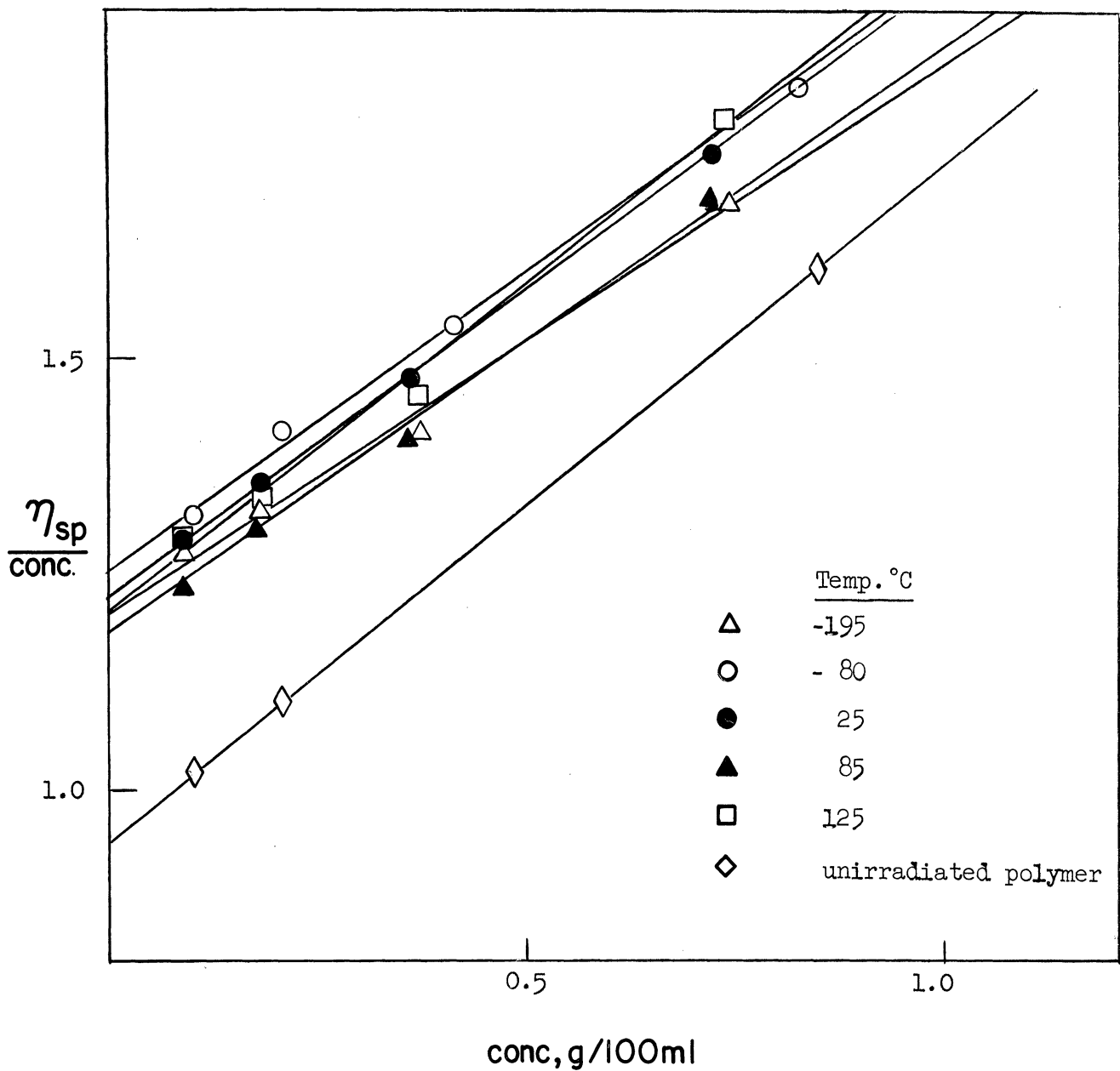


Figure 13. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-bromostyrene on the temperature of the irradiation, at a total dose of  $0.05 \times 10^6$  R.



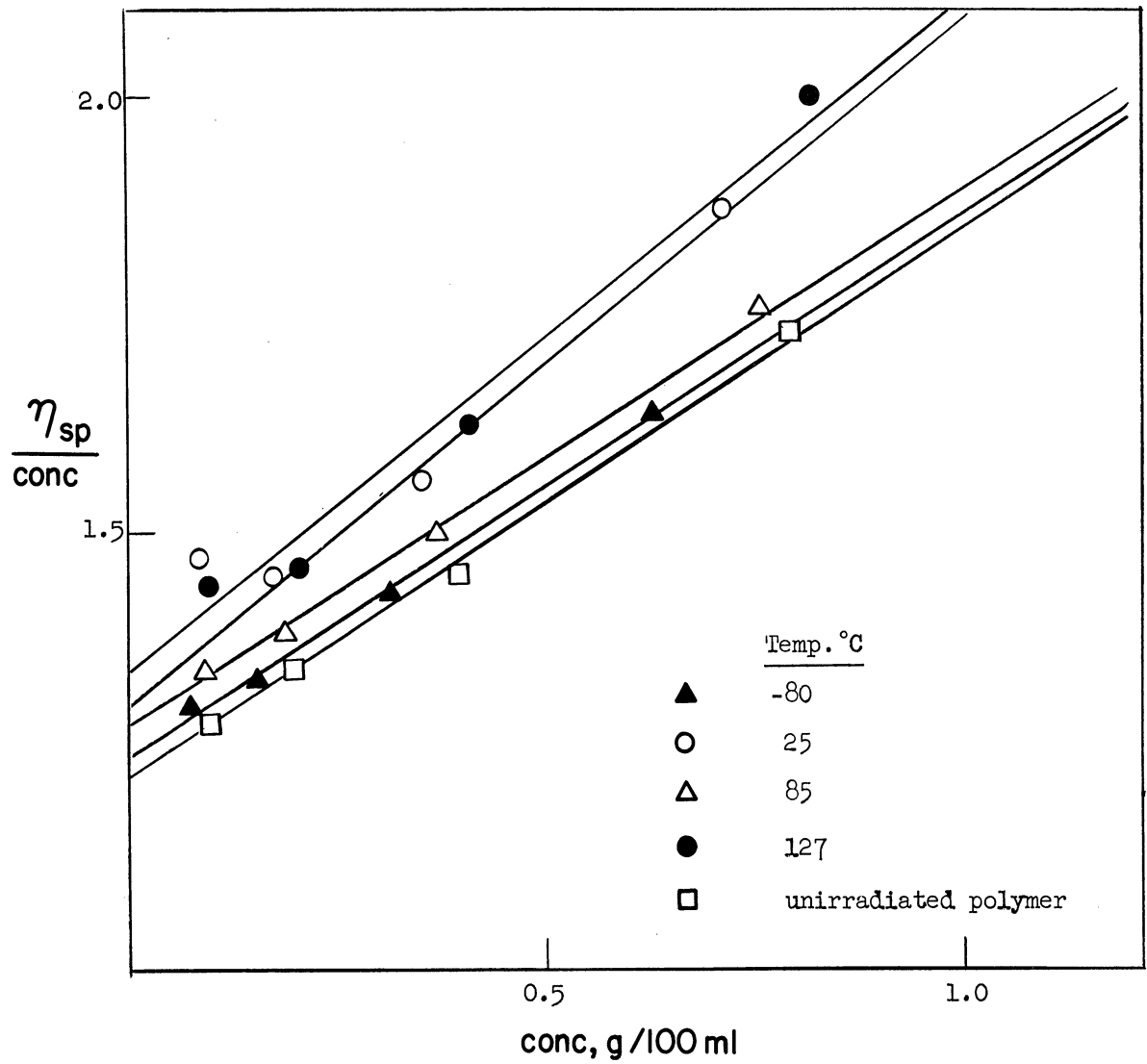


Figure 14. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-bromostyrene on the temperature of the irradiation, at a total dose of  $0.93 \times 10^6$  R.

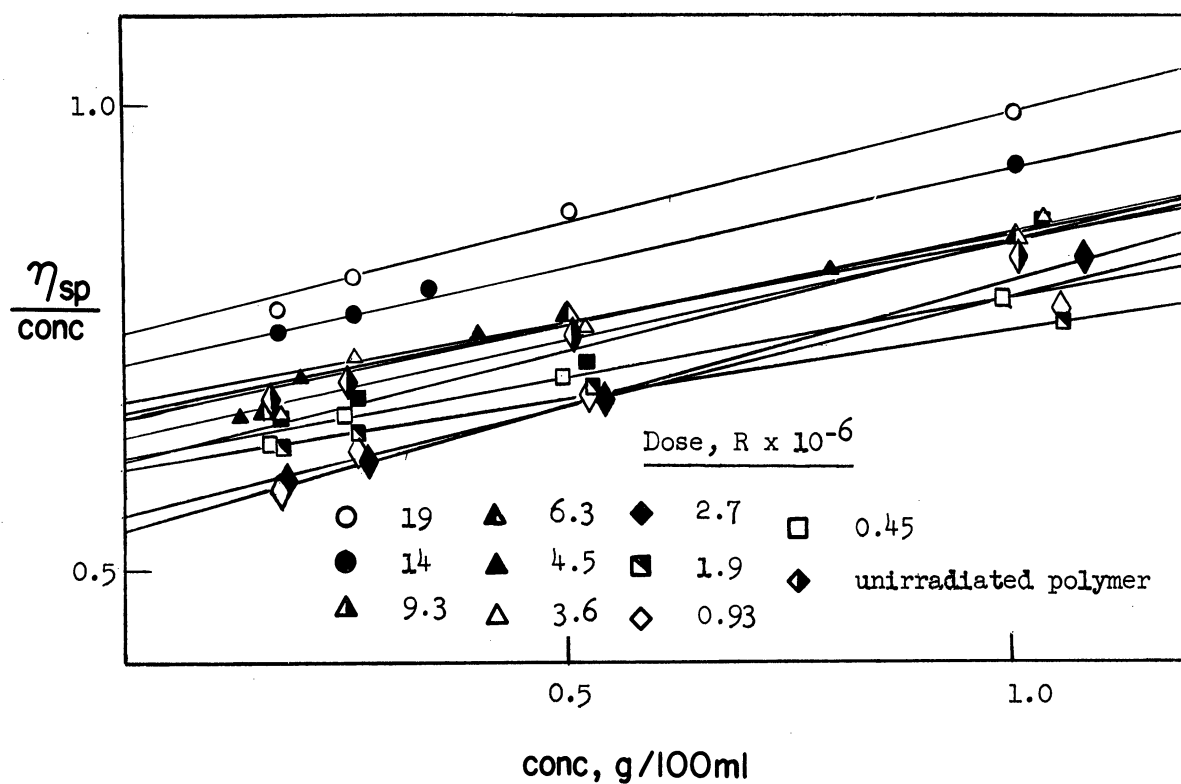


Figure 15. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-cyanostyrene on the total dose, at 25°C.

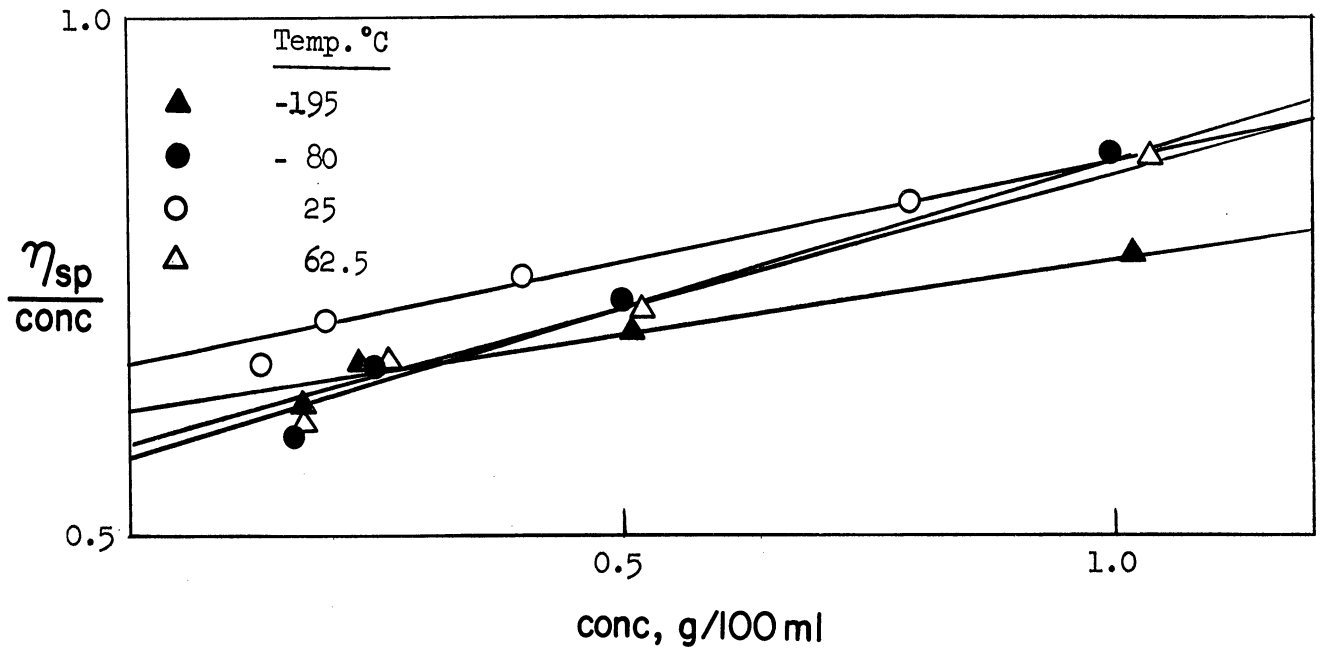


Figure 16. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-cyanostyrene on the temperature of the irradiation, at a total dose of  $4.5 \times 10^6$  R.

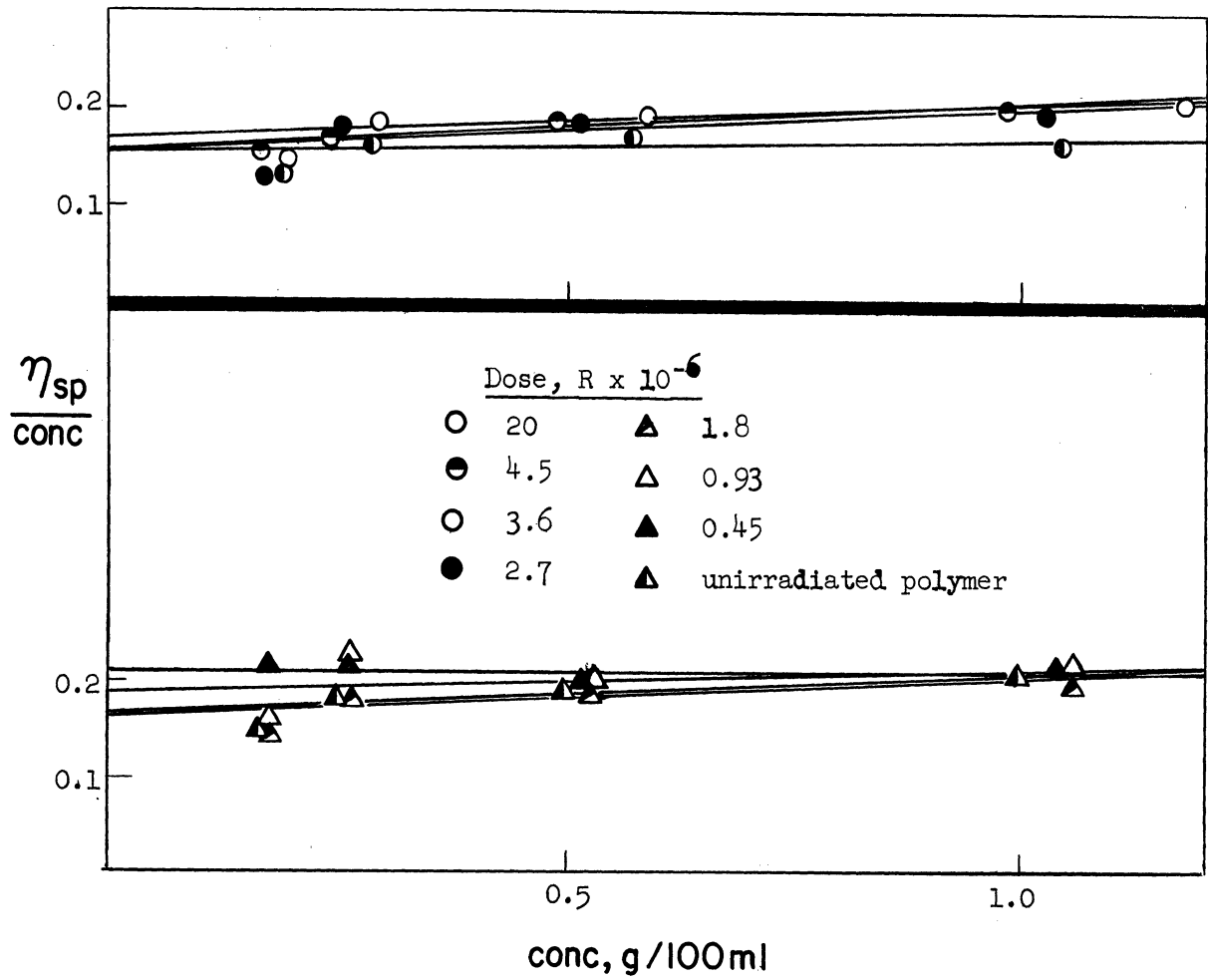


Figure 17. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-nitrostyrene on the total dose, at a temperature of 25°C.

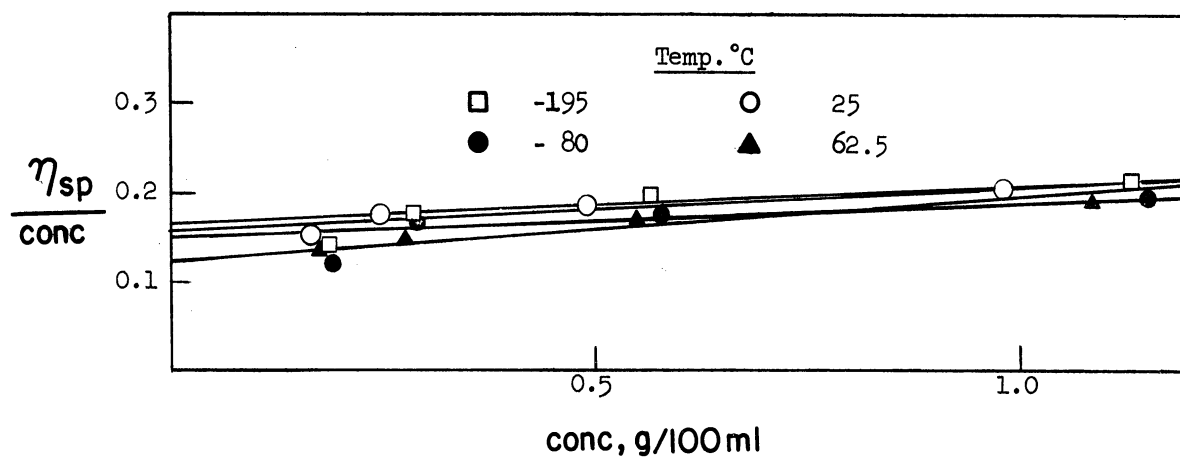


Figure 18. Dependence of  $[\eta]$  of  $\gamma$ -irradiated poly-p-nitrostyrene on the temperature of the irradiation, at a total dose of  $4.5 \times 10^6$  R.

TABLE XI  
EFFECT OF DOSE ON G(CROSSLINK) FOR  
p-SUBSTITUTED POLYSTYRENES<sup>a</sup>

Dose, Rx10 <sup>-6</sup>	G(crosslink)						
	-OCH <sub>3</sub> (3.3x10 <sup>5</sup> ) <sup>b</sup>	-CH <sub>3</sub> (3.7x10 <sup>5</sup> )	-H (2.5x10 <sup>5</sup> )	-Cl (3.8x10 <sup>5</sup> )	-Br <sup>c</sup> (4.2x10 <sup>5</sup> )	-CN <sup>f</sup>	-NO <sub>2</sub> <sup>g</sup>
0.45	0	0.042		0	5.0 <sup>d</sup>		
0.93	0			0.016	2.0 <sup>e</sup>		
1.9	0	0.055	0.050	0.084			
2.7	0.024	0.067		GEL			
4.5	0.081	0.0930					
3.6	0.054	0.057					
6.3	0.082	0.076					
9.3	0.080	0.070	0.051				
12.0	0.071						

- (a) Dose rate,  $2.3 \times 10^5$  R/hr. at 25°.  
 (b) Figures in parentheses indicate the initial molecular weight.  
 (c) This polymer gels at  $0.15 \times 10^6$  R. Doses, R, employed:  
 (d)  $0.05 \times 10^6$ .  
 (e)  $0.10 \times 10^6$ .  
 (f) This polymer exhibited no change in  $[\eta]$ , within experimental error, up to a dose of about  $20 \times 10^6$  R.  
 (g) This polymer did not gel at a dose of  $100 \times 10^6$  R.

to crosslinking, electron releasing groups do not alter the crosslinking tendency. However, if one examines the plots of  $[\eta]$  vs. total dose for the systems studied, it is seen that for both the p-methyl- and p-methoxypolymers, as irradiation continues, branching increases markedly. The formation of branched structures is indicated by the changing slopes of the viscosity-curves, and is manifested in increasing values of Huggins' constant,  $k'$  (summarized in Table XII) as the dose is increased. Thus it appears that in the case of the latter polymers, more sites are available at which crosslinking can occur. It should be emphasized that

the precise relation of polymer structure on  $k'$  is unknown at present, so that these data merely suggest increased branching.

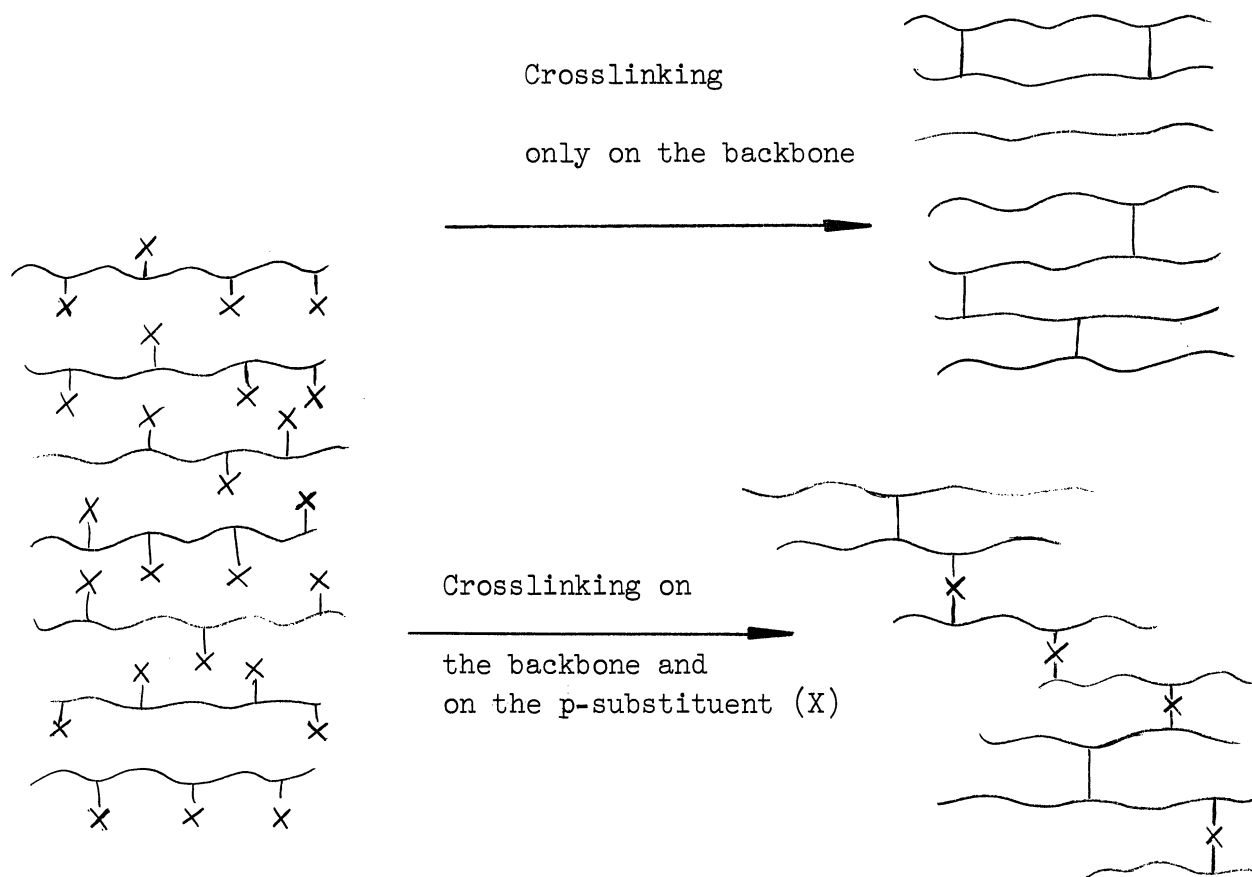
TABLE XII

HUGGINS' CONSTANT,  $k'$ , FOR THE  $\gamma$ -IRRADIATION OF POLY-p-METHYLSTYRENE AND POLY-p-METHOXYSTYRENE<sup>a</sup>

Substituent	Dose	$k'$
p-OCH <sub>3</sub>	0	0.325
	0.45 x 10 <sup>6</sup>	0.325
	0.93 x 10 <sup>6</sup>	0.325
	1.9 x 10 <sup>6</sup>	0.325
	2.7 x 10 <sup>6</sup>	0.325
	3.6 x 10 <sup>6</sup>	0.325
	4.5 x 10 <sup>6</sup>	0.325
	6.3 x 10 <sup>6</sup>	0.363
	9.3 x 10 <sup>6</sup>	0.384
12.0 x 10 <sup>6</sup>	0.358	
p-CH <sub>3</sub>	0	0.071
	0.45 x 10 <sup>6</sup>	0.071
	0.93 x 10 <sup>6</sup>	0.071
	1.9 x 10 <sup>6</sup>	0.071
	2.7 x 10 <sup>6</sup>	0.071
	3.6 x 10 <sup>6</sup>	0.071
	6.3 x 10 <sup>6</sup>	0.397
	9.3 x 10 <sup>6</sup>	0.274

- (a) Temp. of irradiation, 25°; the slopes of the p-Br, p-Cl, p-NO<sub>2</sub> and p-CN polystyrenes were constant and independent of the irradiation dose.

However, data on H<sub>2</sub> yields of these two polymers clearly suggest that C-H bond breakage also takes place on the substituent itself; it is reasonable, therefore, to postulate that additional sites for crosslinking in the p-methyl and p-methoxy polymers are formed on the p-substituent, perhaps even more readily than on the backbone. The structural changes for these polymers may be represented schematically as follows:



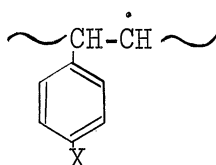
That the ring is not directly involved in the crosslinking process for unsubstituted polystyrene is concluded from studies on the crosslinking sensitivity of the  $p\text{-d}_1$ -polymer;<sup>(8)</sup> the absence of halogen and nitrogen compounds from the correspondingly substituted polymers indicates the absence of substituent participation in the crosslinking process for these materials.

Thus from  $G(\text{crosslink})$  data, and in light of the direct participation of the  $-\text{CH}_3$  and  $-\text{OCH}_3$  groups in the crosslinking step, one can qualitatively conclude that when compared with the unsubstituted polystyrene, both electronegative and electropositive substituent decrease the  $\gamma$ -ray sensitivity of the backbone chain.



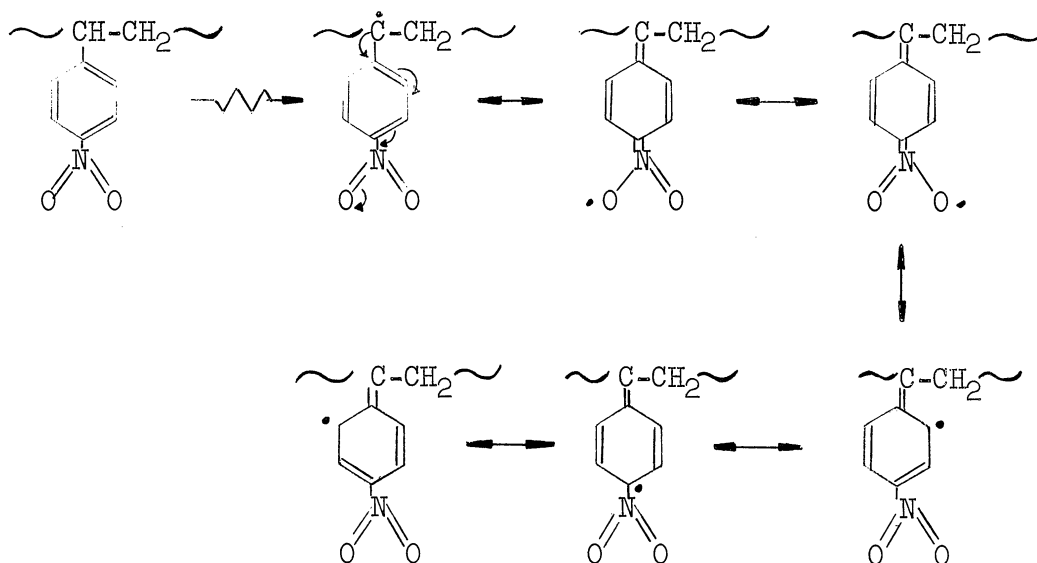
While sufficient data are unavailable to clearly establish whether ionic or radical species are involved in the crosslinking step, it might be expected that an ionic mechanism would be markedly sensitive to the polar environment about the reacting site. That such sensitivity to positive and negative sites is not noted is an indication that free radicals are of importance in the crosslinking step. Thus, it is suggested that radiation initiated crosslinking is a free radical process and that the stability of the intermediate polymer radical formed upon  $\gamma$ -irradiation is of prime importance in determining the ease with which crosslinking occurs. Thus, for crosslinking to take place, two macro-radicals must approach closely enough for bond formation to occur, and the electrons must be available for pairing. Any substituent in the p-position will delocalize a free electron on the  $\alpha$ -carbon atom of the backbone (thus making it unavailable for reaction) by resonance interaction through the benzene ring involving o- and p-quinoid structures.

The stability of this intermediate radical will also be reflected in the crosslinking susceptibility if motion of a radical site along the chain to a suitable environment is necessary for the formation of a crosslink. Thus, radical site migration depends on successive jumps of adjacent H atoms to the carbon atom possessing the unpaired electron; the rate of such jumps will depend on the relative reactivity of the starting radical and that of the product. In the case of H transfer from this  $\beta$ -carbon atom to the  $\alpha$ -carbon atom, the product would have a structure such as

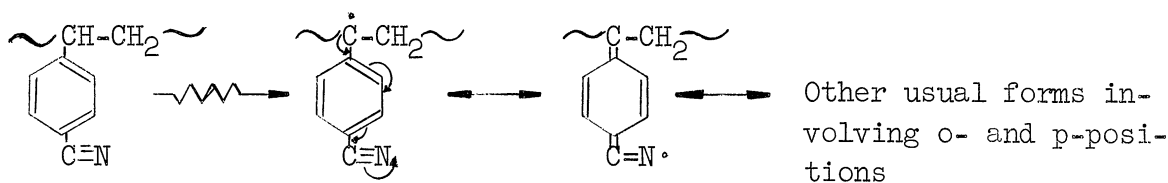


which is not resonance stabilized. Thus, thermodynamically, H atom migration from a  $\beta$ -carbon to an  $\alpha$ -carbon is not favored.

A radical site initially produced on the  $\beta$ -carbon will not be resonance stabilized, for resonance effects are not transmitted over more than one carbon atom, although by a simple  $H\cdot$  transfer, the radical site can "migrate" to the  $\alpha$ -carbon. Compared with the unsubstituted polystyryl radical, resonance stability is greatly enhanced by the strongly electronegative  $-NO_2$  and  $-CN$  groups; examination of the contributing forms which may be written for these polymer radicals shows the great degree of participation of the p-groups in the resonance structures:

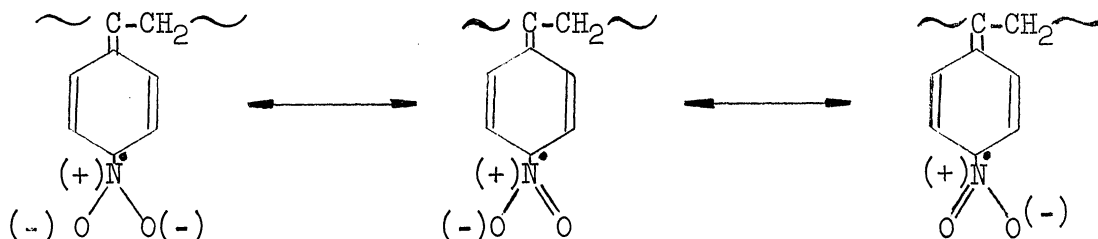


Some Resonance Forms of the Poly-p-Nitrostyryl Radical



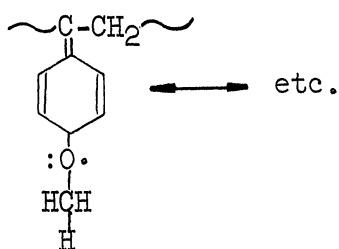
Some Resonance Forms of the Poly-p-Cyanostyryl Radical

Superimposed on each of these radical-resonance structures, of course, are the normal "separation of charge" contributing forms, e.g., for the p-NO<sub>2</sub> derivative, one may write:



As irradiation proceeds, a steady state concentration of poly-p-nitro- and poly-p-cyanostyryl radicals is reached; at this stage, recombination of the polymer radical with H $\cdot$  occurs so that the observed H<sub>2</sub> yield is significantly less than that noted for the remaining polymers (again, other than the p-halopolymers).

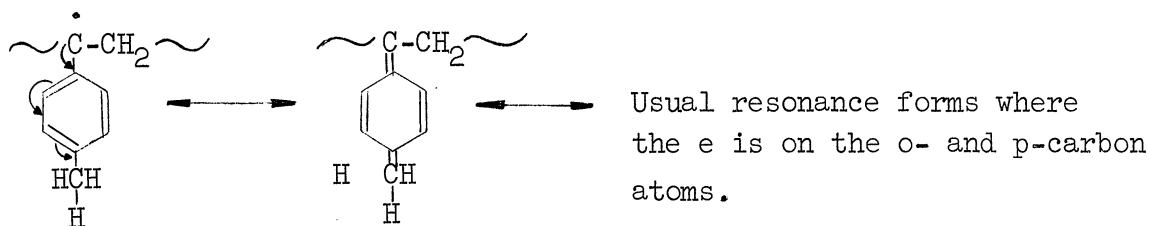
In the p-OCH<sub>3</sub> polymer the oxygen atom offers an additional site for the odd electron, (in addition to the o- and p-positions) and this radical, too, is



more resonance stabilized than the unsubstituted polystyryl species.

The surprisingly large stabilizing effect of the p-CH<sub>3</sub> group on the macroradical cannot be explained by resonance alone and contributing hyper-conjugative structures<sup>(68)</sup> such as the following must be

considered:



It is known that steric factors alter the importance of the resonance contribution to the stability of free radicals; examination of molecular models of the p-substituted polystyrenes, however, indicate that for these systems, the steric effect can be neglected safely (Figure 3).

## 2. Poly-p-Bromo- and Poly-p-Chlorostyrenes

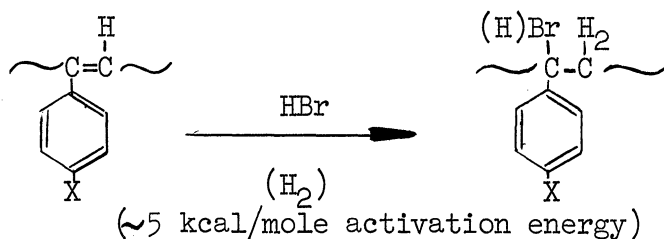
The overall stability of the p-halopolymer radical is the resultant of two electronic phenomena: (a) the electronegativity of the atoms, tending to pull electrons from the ring and (b) the availability of an unshared pair of electrons on the halogen capable of interacting with the ring. The net effect of these opposing forces, however, is probably still enhanced stability of the odd electron, although the magnitude of such stabilization relative to polystyryl radicals cannot be estimated at present. In any event, the p-halopolystyrenes gel at the dose of  $4.6 \times 10^6$  R employed for the other systems; G(crosslink) were therefore determined at doses of  $4.6 \times 10^4$  R and  $0.93 \times 10^5$  R for the bromo- and chloropolymers, respectively. Radical stability does not appear to be of prime significance for these polymers.

The inordinately high sensitivity of the p-halostyrenes at doses an order of magnitude lower than those employed for the other polymers,

as well as the absence of halogen containing molecules in the gases produced upon irradiation can be explained in terms of a free radical chain reaction (leading to crosslinking) initiated by  $\gamma$ -induced cleavage of the aromatic C-halogen bond. The  $\text{Br}\cdot(\text{Cl}\cdot)$  resulting from this initial bond breaking is capable of easily abstracting a  $\text{H}\cdot$  from the polymer chain; this step increases the concentration of radical sites and thus favors the crosslinking process. Evidence from gas yields of deuterated polymer clearly indicate that radical abstraction, not radical recombination in the gas phase, is the fate of the initially formed radical.

The  $\text{HBr}(\text{HCl})$  so formed is much more radiation sensitive than any of the other gases which may be produced by  $\gamma$ -bombardment, and it is postulated that this molecule under the conditions of the reaction, can decompose rather easily into  $\text{H}\cdot$  and  $\text{Br}\cdot(\text{Cl}\cdot)$ .

As  $\text{HBr}$  is formed, and the subsequently produced  $\text{Br}$  atoms continue to abstract  $\text{H}$  atoms, the concentration both of unsaturated sites,  $\text{HBr}$  and perhaps  $\text{H}_2$  increases. It is seen that if hydrobromination or hydrogenation of these double bonds occurs (and these are well known organic reactions) according to the following route:



relatively little  $\text{H}_2$  will be detected in the effluent gases. Low  $G(\text{H}_2)$  values observed for these polymers are in accord with this scheme. Furthermore, as this chain reaction continues, the number of sites available for

crosslinking is not significantly diminished because of the continuous formation of saturated sites again susceptible to abstraction of H or Br, leading to crosslinking.

It is conceivable that the H $\cdot$  initially formed from cleavage of the bonds in the main chain can abstract Br $\cdot$ (Cl $\cdot$ ) from the p-position. The net effect, i.e., the formation of a high concentration of radical sites on the polymer via Br $\cdot$ (Cl $\cdot$ ) abstraction reactions is the same for both processes. While it is not possible to distinguish between the two, initial C-Br (C-Cl) cleavage is more likely on the basis of bond strengths.

A free radical chain reaction mechanism has been proposed for the e-induced dehydrochlorination of polyvinyl chloride; the predominant primary process is the formation of (Cl $\cdot$ ).

### 3. Temperature Dependence of Crosslinking

In the temperature range from  $-200^{\circ}$  to  $25^{\circ}$ , for all but two of the polymers, G(crosslink) was essentially independent of the temperature. Such behavior is reported for G(crosslink) for polystyrene<sup>(7)</sup> and for styrene-methyl methacrylate copolymers,<sup>(9)</sup> and low apparent activation energies are to be expected for such reactions.

On the other hand, G(crosslink) for poly-p-methylstyrene ( $4.5 \times 10^6$  R) at  $-200^{\circ}$ ,  $-80^{\circ}$  and  $25^{\circ}$  are 0.01, 0.04, 0.07, respectively; for the p-chloropolymer, ( $2.7 \times 10^6$  R), G(crosslink) at these temperatures are 0.04, 0.03 and gel, respectively. No explanation is offered for these phenomena.

At temperatures approaching  $100^{\circ}$ , the extent of crosslinking decreased significantly, or degradation was noted for all the polymers. This

is attributed, to some extent, to pyrolysis of the polymers, which normally occurs about 50° higher in the absence of radiation. Radiation effects at temperatures greater than room temperature were not studied in further detail; nevertheless, it is tempting but not possible at present, to relate the temperature dependence of the crosslinking step to the second order transition temperature of the polymer. The polystyrenes studied all have second order transition temperatures between 80-120°. It is of par-enthetic interest that a separate study of the temperature dependence is under way for polyalkyl acrylates; the latter compounds having second order transition temperatures of -70° to 25° are easily available.

#### D. Dose for Incipient Gelation

##### Calculation of G(Crosslink)

Theory states<sup>(61)</sup> that whatever the initial molecular weight distribution, gelation begins when there is formed 1 crosslink per weight average molecule. The dose for incipient gelation, therefore, depends on the molecular weight and molecular weight distribution of the sample. Thus at the gel point, which can be determined experimentally as described in the EXPERIMENTAL section above, the fraction of main chain units crosslinked ( $q$ ; also called the crosslink density) and the weight average degree of polymerization ( $u_2$ ) are related by the expression

$$qu_2 = 1 \quad (A)$$

If it is assumed (as numerous experiments indicate) that the crosslink density  $q$  depends only on the radiation dose for gelation,  $r_{gel}$ , and is independent of the dose rate, then

$$q = q_0 r_{gel},$$

where  $q_0$ , which is a constant describing the crosslinking susceptibility of a polymer, is the fraction of monomer units crosslinked per unit radiation dose. Equation (A) then becomes:

$$q_0 r_{gel} u_2 = 1$$

or

$$r_{gel} = \frac{1}{q_0 u_2} \quad (B)$$

If both sides of Equation (B) are multiplied by the molecular weight of the monomer unit,  $w$ , and by  $u_2$ , there is obtained:

$$r_{gel} (M_w) = \frac{w}{q_0}$$

where  $M_w$  is the weight average molecular weight of the polymer. If the radiation dose  $r$ , is expressed in rads  $\times 10^{-6}$ , and if it is assumed that a dose of  $0.93 \times 10^6$  rads is accompanied by the absorption of  $58 \times 10^{18}$  ev per gm of polymer, and that the  $G(\text{crosslink})$  is independent of the polymer molecular weight,

$$(G) (r_{gel}) (M_w) = 0.48 \times 10^6 \quad (C)$$

Equation (C) affords another method (not an independent means, since susceptibility to crosslinking of course parallels susceptibility to gelation for determining  $G(\text{crosslink})$ ).

This equation, derived by Charlesby,<sup>(2)</sup> has been verified in this laboratory for polystyrene gelled under the conditions described for this study and is in accord with published,<sup>(7)</sup> experimentally determined  $G(\text{crosslink})$  values for polystyrene based on measured molecular weight changes. This agreement between experiment and theory also indicates the validity



of the assumption that the weight average molecular weight is twice the number average molecular weight. Table XIII summarize the dependence of D, determined from solubility data (Figure 19), on the  $\beta$ -substituent and lists G(crosslink) obtained from Charlesby's equation and the experimentally determined D.

TABLE XIII  
DEPENDENCE OF G(CROSSLINK) AND THE DOSE D,  
FOR INCIPIENT GELATION,<sup>a</sup> ON THE p-SUBSTITUENT

	D., R x 10 <sup>-6</sup>	G(Crosslinks)
p-Br	0.15	4.0
p-Cl	3.0	0.2
p-CH <sub>3</sub>	11.0	0.07
p-OCH <sub>3</sub>	14.0	0.05
p-H	25 <sup>b</sup> ; (10 <sup>c</sup> )	0.04
p-NO <sub>2</sub>	> 100	< 0.009 <sup>d</sup>
p-CN	> 100	< 0.009

(a) all at 25°; (b) data from this work;  
(c) data from Ref. 5; (d) assuming a  
weight average molecular weight of 5.0 x 10<sup>5</sup>.

Well within experimental error, these data again indicate the sensitivity of the halopolymers to crosslinking and suggest that initial radical formation via cleavage of a C-halogen bond followed by a chain reaction (page 70), is a significant step in the mechanism. If it assumed again that the p-CH<sub>3</sub> and p-OCH<sub>3</sub> groups, in addition to the backbone chain, are loci for crosslinking, the order of sensitivity to gelation parallels that obtained from  $\gamma$ -initiated crosslinking data. It is suggested that the stability of the intermediate radical formed as a result of resonance with the p-substituent also explains the relative

sensitivity to gelation; thus, a stabilized radical will have little tendency to react, while the more active radicals will enter into such crosslinking reactions.

The lack of correlation both of crosslinking and gelation data with the Hammett  $\sigma$ - $\rho$  scheme, as indicated in the section of gas yields, is further indirect proof of the importance of resonance stabilized intermediates in these processes.

Both techniques employed to determine  $G(\text{crosslink})$ , i.e., estimation from measurements of increasing molecular weight in the pre-gel region and from measurements of the dose for incipient gelation (Figure 19), should yield the same  $G$ -values. Inspection of Tables XIII and XI indicate that this in fact is so for all the polymers but the *p*-chloro-polystyrene. In light of the errors inherent in the measurement of  $G(\text{crosslink})$ , the discrepancy is explained by assuming that molecular weight increases at the doses studied were too low to permit precise determination of the  $G$ -values; increases in chain length at somewhat higher doses, but under  $2.7 \times 10^6$  R were not measured.

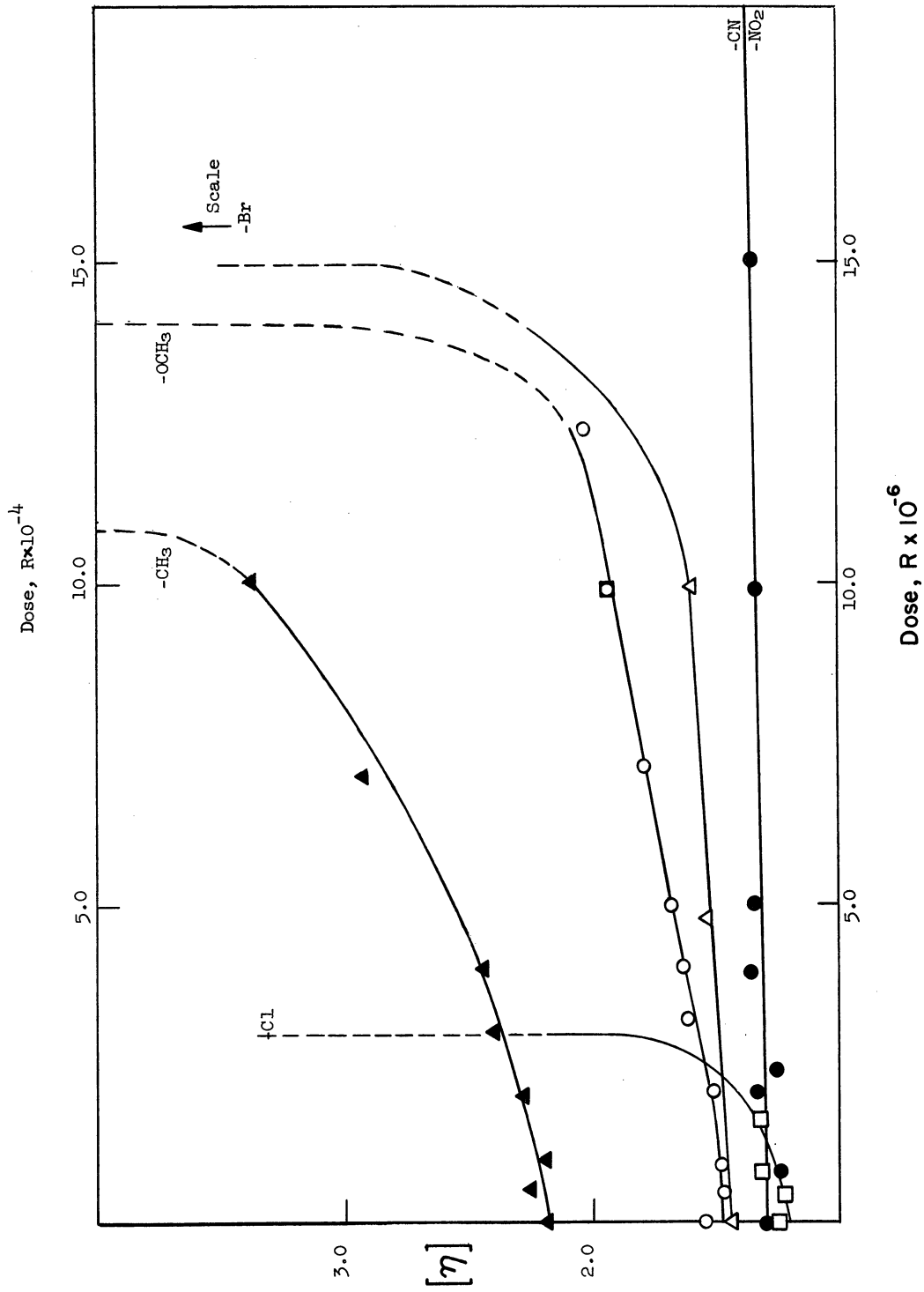
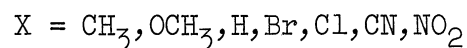
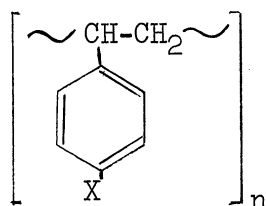


Figure 19.  $[\eta]$ -dose curves used to determine the dose for incipient gelation. Poly-p-introstyrene exhibited no change in  $[\eta]$  after a dose of  $100 \times 10^6$  R.

#### IV. SUMMARY OF CONCLUSIONS

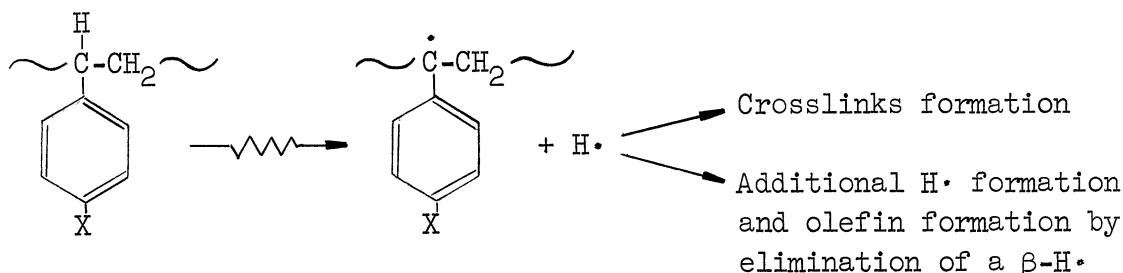
$\gamma$ -Irradiation (at dose of the order of  $10^5 - 10^6$  R) of p-substituted polystyrenes of the following structures



$n \cong 2500$

result in the formation of  $\text{H}_2$ , crosslinks and ultimately gel.

On the basis of values of  $G(\text{H}_2)$  and  $G(\text{crosslink})$ , and the absence of correlation of these data with the Hammett  $\sigma$ - $\rho$  scheme, it is concluded that in general, resonance stabilization of the intermediate polymer radical formed when these polymers are irradiated is responsible for the observed radiation effects.



The backbones of all the polymers thus, liberate less  $\text{H}_2$ , and, except for the p-halopolymers, crosslink to a lesser extent than unsubstituted polystyrene; in fact, the p-nitro polymer does not gel at a dose five-fold greater than that required to produce gel in polystyrene.

For some systems, namely the p-bromo- and p-chloropolystyrenes, the inordinately high sensitivity to crosslinking noted suggests that a

chain reaction involving the radiation susceptible C-halogen bond is an important factor in the radiation chemistry. The relatively low  $G(H_2)$  values observed for these polymers are in accord with the suggestion that, as irradiation proceeds, some hydrogen (as HBr or  $H_2$ ) react with the double bonds of the polymer.

## BIBLIOGRAPHY

1. Bovey, F. "Effects of Ionizing Radiation on Polymers." Interscience Publishers, New York, 1958.
2. Charlesby, A. "Radiation Effects in Materials." Pergamon Press, New York, 1960.
3. Charlesby, A. J. Polymer Science, 11, 513 (1953).
4. Charlesby, A. J. Polymer Science, 11, 521 (1953).
5. Shultz, A., Roth, P. and Rathmann, G. J. Polymer Science, 22, 495 (1956).
6. Feng, P. and Kennedy, J. J. Am. Chem. Soc., 77, 847 (1955).
7. Wall, L. and Brown, D. J. Phys. Chem., 61, 129 (1957).
8. Burlant, W., Am. Chem. Soc. Meeting, September, 1960, New York.
9. Burlant, W., Green, D. and Taylor, C. J. Applied Polymer Science, 1, 296 (1959).
10. Alexander, P. and Toms, D. J. Polymer Science, 22, 343 (1956).
11. Wall, L. and Brown, D. J. Res. Nat. Bur. Stds., 57, 131 (1956).
12. Alexander, P., Black, R. and Charlesby, A. Proc. Roy. Soc. (London), A232, 31 (1955).
13. Wall, L. and Florin, R. J. Appl. Polymer Sci., 2, 251 (1959).
14. Sisman, O. and Bopp, C., ORNL, 928 (1951).
15. Bopp, C. and Sisman, O. Nucleonics, 14, (3), 52 (1956).
16. Charlesby, A. Proc. Roy. Soc., A215, 187 (1952).
17. Weiss, J. J. Polymer Sci., 29, 425 (1958).
18. Dole, M. and Kelling, C. J. Am. Chem. Soc., 75, 6082 (1953).
19. Dole, M., Keeling, C. and Rose, D. J. Am. Chem. Soc., 76, 4304 (1954).
20. Pearson, R. Chem. and Ind., 903 (1956).
21. Pearson, R. Chem. and Ind., 209 (1957).
22. Pearson, R. J. Polymer Sci., 25, 189 (1957).

23. Warner, A., Muller, F. and Nordlin, H. J. Appl. Phys., 25, 131 (1954).
24. Mayburg, S. and Lawrence, W. J. Appl. Phys., 23, 1006 (1952).
25. Bohn, D., RRC Technical Report 3, July, 1951, as seen in Reference 2.
26. Fowler, J. and Farmer, F. Nature (London), 171, 1020 (1953).
27. Fowler, J. and Farmer, F. Nature (London), 173, 317 (1954).
28. Fowler, J. and Farmer, F. Nature (London), 174, 136 (1954).
29. Fowler, J. and Farmer, F. Nature (London), 174, 800 (1954).
30. Fowler, J. and Farmer, F. Nature (London), 175, 516 (1955).
31. Fowler, J. and Farmer, F. Nature (London), 175, 590 (1955).
32. Fowler, J. and Farmer, F. Nature (London), 175, 648 (1955).
33. Fowler, J. and Farmer, F. Brit. J. Radiol., 29, 338 (1956).
34. Fowler, J. Proc. Roy. Soc., A236, 464 (1956).
35. Charlesby, A. Proc. Roy. Soc., A231, 521 (1955).
36. Wall, L. J. Polymer Sci., 17, 141 (1955).
37. Alexander, P., Charlesby, A. and Ross, M. Proc. Roy. Soc. (London), A223, 392 (1954).
38. Lawton, E., Balwit, J. and Powell, R. J. Polymer Sci., 32, 257 (1958).
39. Lawton, E., Balwit, J. and Powell, R. J. Polymer Sci., 32, 277 (1958).
40. Burlant, W. and Hoffman, A. Block and Graft Polymers. Reinhold Publishing Corp., New York, 109 (1960).
41. Miller, A., Lawton, E. and Balwit, J. J. Polymer Sci., 14, 503 (1954).
42. Charlesby, A. and Lloyd, D. Proc. Roy. Soc., A249, 51 (1958).
43. Charlesby, A. Nature (London), 173, 578 (1954).
44. Bevington, J. and Charlesby, A., Simposio Inter. di Chem. Macrom., La Ric. Scientifica, 1955.
45. Alexander, P. and Tom, D. J. Polymer Sci., 22, 343 (1956).
46. Hammett, L. Physical Organic Chemistry. McGraw-Hill Book Co., 1940.

47. Joffe, H. Chem. Rev., 53, 191 (1953).
48. Wilmarth, K. and Schwartz, N. J. Am. Chem. Soc., 77, 4543 (1955).
49. Tobolsky, A. and Mesrobian, R. Organic Peroxides. Interscience Publishers, 79 (1954).
50. Brown, H. and Okamoto, Y. J. Am. Chem. Soc., 79, 1913 (1957).
51. Russel, G. J. Org. Chem., 23, 1407 (1958).
52. Marvel, C. and Overberger, C. J. Am. Chem. Soc., 67, 2250 (1945).
53. Smith, L. and Hoehn, H. H. J. Am. Chem. Soc., 63, 1175 (1941).
54. Weiss, J. Nucleonics, 10, (7) (1952).
55. Fuhrman, R. and Mesrobian, R. J. Am. Chem. Soc., 76, 3281 (1954).
56. Kern, W. and Bram, D. Makromol, Chemie., 27, 23 (1958).
57. Flory, P. Principles of Polymer Chemistry. Cornell University Press, 312 (1953).
58. Kamath, P. and Haas, H. J. Polymer Sci., 24, 143 (1957).
59. Shornigin, P. and Shorniginia, N. J. Gen. Chem. (USSR), 5, 555 (1935).
60. Reference 2, page 132.
61. Reference 2, page 536.
62. Trotman-Dickenson, A. Gas Kinetics. Academic Press, New York 152 (1955).
63. Reference 62, page 126.
64. Reference 62, page 177.
65. Rice, F. and Herzfeld, K. J. Am. Chem. Soc., 56, 284 (1934).
66. Farkas, A., Ed. Physical Chemistry of Hydrocarbons. Academic Press, New York, 212 (1953).
67. Pauling, L. Nature of the Chemical Bond. Cornell University Press, New York, 157 (1948).
68. Ingold, C. Structure and Mechanism in Organic Chemistry. Cornell University Press, New York, 90 (1953).
69. Neerman, J. Unpublished work.