

A STUDY OF THE CHAIN TRANSFER REACTIONS OF
POLY(METHYL METHACRYLATE) RADICALS WITH
SUBSTITUTED PHENOLS

A Dissertation
Presented to the
Faculty of the Department of Chemistry
College of Arts and Sciences
University of Houston

In partial fulfillment
of the requirements for the degree
Doctor of Philosophy

by
José M. Sosa
August, 1969

Esta obra es la culminación de una
larga y penosa carrera y es dedicada
a mi esposa, a mis padres, a mis
hermanos, y ha otras personas que la
hicieron posible.

Nunca olvidando la vida, la salud, y
la libertad prestada a mi por El Autor
De La Vida.

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ABSTRACT

The chain transfer constants (C_s) of nineteen phenols with poly-(methyl methacrylate) radicals and the extent of retardation (R_e) of the polymerization reaction by these phenols were determined at 50.0°C.

Attempts were made to correlate both C_s and R_e values with previously published antioxidant ratings of the phenols. R_e values correlated well with antioxidant ratings obtained from the oxidation of petroleum and with the oxidation potentials of the phenols. C_s values did not correlate well with antioxidant ratings for disubstituted phenols with bulky ortho substituents or with phenols possessing groups with benzylic hydrogens.

The poor correlation of C_s values with antioxidant efficiencies appears to be due to the inability of the poly(methyl methacrylate) radicals to abstract phenolic hydrogens from phenols with bulky ortho substituents and to the sluggishness of this radical toward phenolic hydrogen atoms. The latter may result in the abstraction of benzylic and phenolic hydrogen atoms at comparable rates. This premise is supported by a poor correlation of C_s values with Hammett σ substituent values, and by the fact that C_s values increase as the bond strength of the benzylic hydrogens decrease.

Polymerization rates of methyl methacrylate in several phenols and the rates of decomposition of azobisisobutyronitrile in the presence of several phenols were also determined. These investigations showed

that phenols affect the rate of decomposition of the initiator, and this may be another factor affecting the correlation of C_s values with antioxidant ratings and with the Hammett parameter. Inhibition times of the polymerization reaction by phenols in the presence of oxygen correlated well with Hammett σ values and indicate that electron donating groups increase the activity of the phenol.

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I. INTRODUCTION

INTRODUCTION

The atmospheric oxidation of organic compounds has been studied by many investigators. Considerable effort has been expended in attempts to explain the primary reactions involved in this process, in attempts to find ways to inhibit the degradative action, and in the evaluation of the efficiencies of inhibitors.

Prior to 1940, investigations dealt primarily with the autoxidation of fats, petroleum, and rubber. As the volume of plastic materials increased to an annual production of multi-billion pounds, interest shifted to the study of these important high molecular weight compounds. Investigations of low molecular weight hydrocarbons and aldehydes, however, have proved to be more fruitful in providing information for the elucidation of the reaction mechanisms and in suggesting compounds that would inhibit the oxidative process.

Several theories developed in the late 1920's attempted to account for the primary reactions of the oxidative process. Most of the proposed mechanistic pathways suggested the formation of peroxy intermediates, but they differed significantly in accounting for the fate of the intermediates and in explaining the action of inhibitors.

The currently accepted mechanism which resulted from the efforts of many investigators is essentially that proposed by Bolland and ten Have (1) in 1947. This has not been altered greatly since that time and represents the present thinking, in part, in this field. This scheme may be summarized as follows:

Initiation: Substrate (RH) $\xrightarrow{A}$ free radicals (R $\cdot$)

Propagation: R $\cdot$ + O $_2$ $\rightarrow$ R-OO $\cdot$

R-OO $\cdot$ + R-H $\rightarrow$ R-OOH + R $\cdot$

Termination: 2 R-OO $\cdot$ $\rightarrow$ products

In the presence of a stabilizer (AH), the inhibition of the chain reaction occurs as a result of the following reactions:

Inhibition: R $\cdot$ + AH $\rightarrow$ RH + A $\cdot$

R-OO $\cdot$ + AH $\rightarrow$ R-OOH + A $\cdot$

The structure of the stabilizer (AH) was found to be of prime importance in determining whether the resultant radical (A $\cdot$) would be effective in preventing additional propagation reactions or termination.

In many studies of autoxidation it was noted that the more efficient inhibitors or "antioxygens" were compounds that were readily oxidized. One of the earliest useful observations of antioxidant activity was made by Moureau and Dufraisse (2) in 1922. While studying the oxidation of benzaldehyde by the oxygen absorption technique, they noted that no oxygen was absorbed when phenol was present. Bickel and Kooyman (3) investigated the autoxidation of several hydrocarbons in the presence of substituted phenols in greater detail and observed that inhibition of the oxidation reaction depended markedly

on the structure of the phenols. These workers carried out a similar study (4) using several amines and arrived at the same conclusion.

These and many other investigators suggested the types of antioxidants that could serve as stabilizers to prevent the deterioration of foodstuffs, oils, and polymeric materials. Although a wide variety (5) of antioxidants is available, only one class of antioxidants is considered here. Antioxidants, such as hindered phenols and some aromatic amines are widely used and are often referred to as chain stoppers or radical interceptors. These compounds possess labile hydrogen atoms which when abstracted yield radicals that are poor chain initiators. However, only phenolic antioxidants were considered in this investigation.

The antioxidant efficiency of phenolic derivatives may be measured by following the rate of oxygen absorption of tetralin or some other hydrocarbon in the presence of the antioxidant. Antioxidant efficiencies have also been measured by noting the length of the inhibition period during the oxidation of a hydrocarbon in the presence of the antioxidant. Studies using these techniques have provided most of the available data on antioxidant efficiencies.

Attempts have also been made to correlate antioxidant efficiencies (6) with the oxidation potentials and the OH stretching frequencies of phenols, however, neither correlation has provided a basis for generalization to date.

Previous investigators have recognized the fact that antioxidant efficiencies increase as the AH bond became weaker and as the

stability of the resultant radical ($A\cdot$) increased. Several procedures have been suggested for the evaluation of the strength of the AH bond and for estimating the stability of the ($A\cdot$) radical. Some of the procedures suggested are theoretical and do not correlate well with experimental observations. Since most of the studies attempting to correlate chemical structure with antioxidant efficiency have not been entirely successful, it was the purpose of this study to suggest a different method of obtaining the relative stabilities of phenoxy radicals and the relative labilities of phenolic hydrogens.

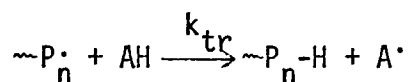
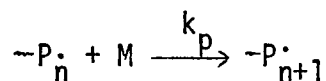
II. THE PROBLEM

THE PROBLEM

Statement of the Problem. It was the purpose of this study

1. to evaluate the chain transfer constants of several phenols and to correlate these constants with the efficiencies of these phenols as antioxidants.
2. to evaluate the extent of retardation of the polymerization by these phenols.
3. to compare this technique with other methods used to correlate chemical structure with antioxidant efficiencies.
4. to examine the chain transfer reaction in an attempt to provide information on the relative labilities of the phenolic hydrogens and on the relative stabilities of the phenoxy radicals.

The Approach. The abstraction of H atoms from AH by a growing polymer radical is called a chain transfer reaction. This reaction competes with the addition step in a polymerization shown below, where $\sim P_n^\bullet$ represents a growing polymer radical containing (n) monomer units and where (M) represents the monomer.



The ratio of the specific rate constants k_{tr}/k_p is the chain transfer constant and can be conveniently evaluated by use of the Mayo equation. Details for the calculation of this constant will be given later.

Assuming that abstraction of hydrogen atoms does not occur elsewhere in the molecule, evaluation of the chain transfer constants (C_s) of a series of phenols yields information on the relative labilities of the phenolic hydrogens. If the resultant radical ($A\cdot$) is less active than the growing polymer radical, then the presence of the compound AH will retard the polymerization reaction by the reduction of the number of radicals active enough to initiate a new chain. Thus, by measuring the extent of retardation of the reaction, information on the relative activities of the phenoxy radicals can be obtained.

Several investigators (7,8,9) have suggested that hydrogen atoms are not abstracted at significant rates from other groups of the molecule. It must be further assumed that no side reactions take place but the validity of this assumption has not been proved.

The chain transfer constants of phenols were determined by the reaction of poly(methyl methacrylate) radicals with these compounds. Methyl methacrylate was selected in this investigation since chain transfer constants for only a few phenols have been reported with this monomer. Thus, this study should provide some important information that was not available heretofore. Another factor considered in the selection of this monomer was the reactivity of the radical which is produced is intermediate between the other common monomers such as styrene and vinyl acetate.

Em

Many attempts have been made to correlate the structure of phenols with antioxidant efficiencies using the oxygen absorption technique and the results of several excellent studies are available. The results of this investigation have been compared with some of these previous studies. These comparative results along with some of the previous studies will be discussed in subsequent sections.

Significance of the Study. Many significant discoveries have been made in this field and the literature on this subject is voluminous. Yet there are many deficiencies in the present theories. Hence, there is an opportunity to make improvements on many of these theories. Also, new materials that require different stabilizers are being produced commercially and novel applications for the present stabilizers are being found. A better understanding of the relationship between chemical structure and antioxidant efficiency would aid in the selection of the most suitable stabilizers for specific end uses. This investigation is intended as a short-range study in the field of stabilization and may be correlated in part with long-range studies that are being made in commercial laboratories.

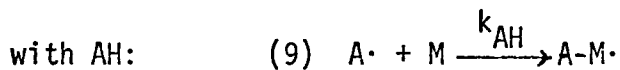
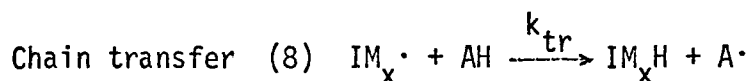
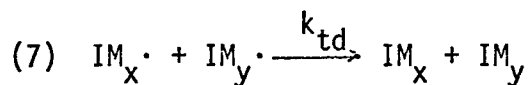
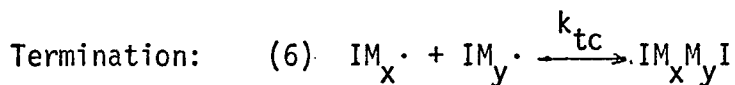
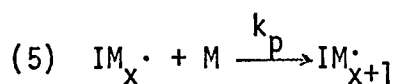
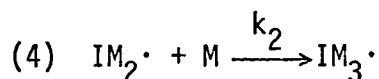
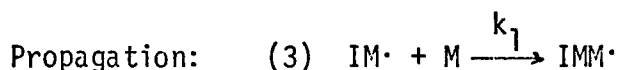
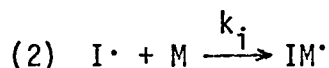
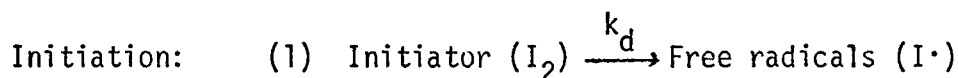
III. REVIEW OF THE LITERATURE

REVIEW OF THE LITERATURE

A. Chain Transfer Reactions

1. The Reaction

The term chain transfer was coined by Flory (10) in 1937. The chain transfer reaction was proposed to explain the fact that products from solution polymerizations had lower molecular weights than those from bulk polymerizations. Flory postulated that the growing polymer radical abstracted a hydrogen atom from the additive (AH) and created a new radical (A·) that could initiate a new chain. The following kinetic scheme represents the chain polymerization reaction.



The chain transfer reaction proposed by Flory is the reaction that Bolland and ten Have consider as the inhibition step in their proposed oxidation mechanism provided that the resultant radical ($A\cdot$) is a poor chain initiator. In the reaction proposed by Flory, it was assumed that the resultant radical was active enough to initiate a chain because the rate of polymerization was not affected significantly when the reaction was carried out in common solvents.

2. The Mayo Equation

Polymer technologists have used this reaction to control the molecular weight of synthetic polymers. Mercaptans, aldehydes, and some hydrocarbons are used routinely in controlling the molecular weights of styrene-butadiene rubbers, polyethylene, and other polymeric materials. The effectiveness of an organic compound as a chain transfer agent can be evaluated if the ratio of k_{tr}/k_p is known (Equations 5 and 8). As has been mentioned previously, this ratio can be evaluated by means of the Mayo equation. The derivation of this equation is considered in the following paragraphs.

The average kinetic chain length (v) is defined as the average number of monomers reacting with an active center from its initiation to its termination (11). It can be expressed as the ratio of the rate of the propagation reaction to the rate of initiation ($v = R_p/R_i$). Under the steady-state assumption, the rate of initiation is equal to the rate of termination. Thus, the average kinetic chain length (v) can be expressed as R_p/R_t .

Several investigators have attempted to correlate the kinetic chain length with the average degree of polymerization of the product of a polymerization reaction. The average degree of polymerization ($\bar{P}_n$) is defined as the number of monomer units per polymer chain and is calculated from the molecular weight of the polymer. Tobolsky (12) found that $\bar{P}_n$ was very nearly $2v$ for the polymerization of poly(methyl methacrylate) with certain initiators. Other investigators found that $\bar{P}_n$ was not directly proportional to v when polymerization reactions were carried out in solvents (13) or when high concentrations of the initiators (14) were used. Thus, when $\bar{P}_n$ was not directly proportional to v , it was postulated that other termination reactions were taking place and that the degree of polymerization could be written as follows:

$$(10) \quad \bar{P}_n = \frac{\text{Rate of Polymerization}}{\text{Summation of Rates of Reactions Leading to Termination}}$$

The reactions that can lead to termination of the chain reaction are termination by coupling (tc) and by disproportionation (td); and by chain transfer to monomer (cm), polymer (cp), initiator (ci), and additive (ca). By taking the reciprocal of expression 10, $1/\bar{P}_n$ can be expressed as:

$$(11) \quad \frac{1}{\bar{P}_n} = \frac{R_{tc} + R_{td} + R_{cm} + R_{cp} + R_{ci} + R_{ca}}{R_p}$$

where $R_{\text{subscript}}$ refers to the rate of the specific reactions. Conditions may be chosen such that all other chain transfer reactions except for chain transfer with an additive (ca) are minimized. This is

particularly convenient when a series of additives is considered since all the other termination rates can be assumed to be constant. Under these conditions, equation (11) can be expressed as

$$(12) \quad \frac{1}{\bar{P}_n} = \frac{1}{(\bar{P}_n)_0} + \frac{R_{ca}}{R_p}$$

where $1/(\bar{P}_n)_0$ is the average degree of polymerization when no additive is present. From equations (5) and (8) the rates of propagation and termination due to chain transfer can be obtained and equation (12) becomes equation (13).

$$(13) \quad \frac{1}{\bar{P}_n} = \frac{1}{(\bar{P}_n)_0} + \frac{k_{tr}[IM_x \cdot][AH]}{k_p[IM_x \cdot][M]}$$

Equation (13) can be simplified to yield the Mayo equation (Equation 14).

$$(14) \quad \frac{1}{\bar{P}_n} = \frac{1}{(\bar{P}_n)_0} + \frac{k_{tr}[AH]}{k_p[M]}$$

The ratio of k_{tr}/k_p is the chain transfer constant (C_s). Mayo (15) verified this relationship for several aromatic hydrocarbon solvents at low polymer conversions. Other workers have called this ratio the apparent chain transfer constant when the additives retard the polymerization reaction.

3. Evaluation of Chain Transfer Constants

Equation (14) has been shown to give linear relationships when $[AH]/[M]$ is plotted vs $1/\bar{P}_n$. The slope of this line is the chain

transfer constant. Polymerization reactions are carried out to about 10% yield in sealed ampoules in the absence of oxygen. The reactions may be catalyzed or uncatalyzed. The polymer formed is precipitated from a suitable solvent and the $\bar{P}_n$ can be obtained by several techniques. The most common technique is dilute solution viscometry.

In this technique, use is made of the Mark-Houwink equation which relates the molecular weight of a polymer to the limiting viscosity number $[\eta]$ (Equation 15).

$$(15) \quad M = k [\eta]^\alpha$$

by the constants k and α . The limiting viscosity number can be determined by plotting the viscosity number (n_{sp}/c) vs. concentration (c) and extrapolating to zero concentration (16). A more convenient way is to employ the equation

$$(16) \quad [\eta] = \frac{n_{sp}}{4c} + \frac{3 \ln n_r}{4c}$$

which allows the determination of the limiting viscosity number by a single viscosity measurement (17). The terms used above are defined for capillary viscometers of the Ostwald or Ubbelöhde types as follows:

t = flow time for polymer solution

t_0 = flow time for solvent

t/t_0 = viscosity ratio (n_r)

$t/t_0 - 1$ = specific viscosity (n_{sp})

n_{sp}/c = viscosity number

$\ln n_r$ = logarithmic viscosity number

c = concentration (g/100 ml of solvent)

$\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$ = limiting viscosity number $[\eta]$

Since average molecular weight values obtained by viscometry ($\bar{M}_v$) are higher than number average molecular weights ($\bar{M}_n$), a relationship between the limiting viscosity number and $\bar{M}_n$ is usually used. This is necessary since the degree of polymerization is defined as the average number of monomer units per chain.

4. Important Studies

Several studies that deal with the evaluation of chain transfer constants of phenols have been reported. Most of the constants obtained prior to 1965 are listed in the Polymer Handbook (18). Among the most pertinent studies are those of Godsay and coworkers (19), who evaluated the chain transfer constants of several phenols with polystyryl radicals. An important conclusion from their work is that most simple alkyl phenols do not retard the polymerization reaction effectively and that the Mayo equation can be used to determine their chain transfer constants.

Phenols having bulky ortho substituents were found to retard polymerizations significantly and equations intended to correct for the retardation have been proposed. It was found that the apparent chain transfer constants did not differ greatly from those that were calculated from the Mayo equation. Phenolic compounds having chain

transfer constants greater than 10^{-2} at 60°C were considered to retard the polymerization reaction significantly.

The chain transfer constants for two phenols with poly(methyl methacrylate) which are listed in the Polymer Handbook are as follows:

4-methoxyphenol 5×10^{-4} at 45°C

2,3,4,6-methylphenol 11.0×10^{-4} at 45°C

The chain transfer constants for these compounds with polystyrene at 60°C are 260×10^{-4} and 580×10^{-4} , respectively. These values indicate that in general the chain transfer constants of phenols with poly(methyl methacrylate) are lower than with polystyrene.

Other investigations that are pertinent to this study include the reactions of other radicals with phenolic hydrogens. Ingold (20) investigated the reactions of t-butoxy radicals with phenols and found that the ease of phenolic hydrogen abstraction by these radicals increased when electron donating substituents were present. Correlation of the rates of hydrogen abstraction with Brown's σ^{+} gave a value of -1.19 for ρ . Isotopic studies with 2,6-di-t-butyl-4-methyl phenol (21) indicate that phenolic hydrogen atoms are abstracted approximately 10.6 times faster than phenolic deuterium atoms at 65°C . This reveals that the abstraction of the phenolic hydrogen atom is the rate determining step and suggests that the abstraction of hydrogen atoms from the alkyl group is not significant. Other studies (22) show that electron donating groups increase the effectiveness of phenols as antioxidants.

B. Methods of Correlating Antioxidant Efficiencies

Antioxidant technology progressed rapidly after it was found that phenols inhibited the autoxidation of hydrocarbons and aldehydes. Some of the test methods that have been used to evaluate antioxidants will be discussed. It should be mentioned that the rating given by the following methods is not the sole factor used to determine the suitability of an antioxidant for a specific use since the solubility, toxicity, and volatility of these compounds must also be considered.

The ratings given to several phenols by different investigators using different techniques are summarized in Table I. The ratings given in Columns 1 and 2 were based on data obtained by the oxygen absorption technique. A rating of 100 was assigned to 2,6-di-*t*-butyl-4-methyl phenol. The data in Column 1 were obtained from the oxidation of tetralin (23) and that of Column 2 from the oxidation of petroleum (24). The rating increases as the OH group becomes more sterically hindered and as more electron donating groups are present on the aromatic nucleus. These effects are correlated with the ability of the phenoxy radical to initiate a chain reaction which also decreases as it becomes more sterically hindered and as more electron donating groups are added to the aromatic nucleus.

The rate constants ($1\text{-mole}^{-1} \text{ sec}^{-1}$) of the reactions between phenols and α,α -diphenyl- β -picryl-hydrazyl (DPPH) in carbon tetrachloride at 20°C are summarized in Column 3 (25). These data indicate that electron donating groups have a large influence on the rate constants and that bulky ortho substituents block the availability of the OH

group. The use of this method is limited since many of the better antioxidants are hindered phenols and an accurate evaluation of the strength of the OH bond in these compounds can not be obtained by this method.

G. Gupta and coworkers compared the antioxidant efficiency of phenols as antioxidants with the OH stretching frequency derived from infrared spectroscopy (26)(Column 4). These results indicate that there is no reliable correlation between the force constant and the bond dissociation energy of these compounds. This is due to the fact that the resonance stabilization of the free radical contributes significantly to the bond dissociation energy but not to the calculation of the force constant of the bond.

The relationship between the oxidation potential of phenols and their antioxidant efficiency has been investigated by several workers. Bolland (27) has shown that a linear relationship exists between the oxidation-reduction potential of some non-hindered phenols and their antioxidant efficiency. Penketh (28) also carried out an extensive study on the relationship between the polarographic oxidation potentials of phenols and their effectiveness as antioxidants. Column 5 shows oxidation potentials of several phenols in volts. These values reveal that a correlation does exist and the effectiveness of the compounds as antioxidants increases as the oxidation potential decreases. However, some phenols and amines which have very low oxidation potentials are very poor antioxidants.

G. Gupta and coworkers (26) have also made use of the relationship of antioxidant activity to the bond dissociation energy to suggest

another method of evaluating the efficiencies of phenols as antioxidants. They theorized that the bond dissociation energy should be related to the energy of the most loosely held electron in the compound. A remarkable correlation was obtained when molecular orbital energies calculated by the non-bonding molecular orbital method of Longuet-Higgins and Dewar were compared to antioxidant efficiencies. This was true only for the non-hindered phenols since the method can not account for the decrease in reactivity of the phenoxy radical due to steric hindrance.

In summary, it should be mentioned that probably the most practical and successful method has been the one which measures the induction period. The main objection to this method is that in some cases periods as long as two weeks are required to obtain the necessary information and acceleration of the reaction by higher oxygen pressures and higher temperatures has led to anomalous results (29). Since polymerization reactions are usually carried out in less than three hours, the method proposed in this study does not have this disadvantage.

TABLE I
ANTIOXIDANT RATINGS OF SEVERAL PHENOLS AS GIVEN BY DIFFERENT METHODS

Substituent on phenol	Column				
	1	2	3	4	5
none	4	1	4	3610	0.92
2-methyl	26	14	47	3612	0.85
4-methyl	15	10	55	3610	0.84
2-t-butyl	53	24	--	3609	0.81
4-t-butyl	23	7	83	3614	0.84
2,4-dimethyl	55	47	789	3616	0.76
2,6-dimethyl	56	32	117	3621	0.76
2,6-di-t-butyl	49	--	--	3640	0.68
2,6-di-t-butyl- 4-methyl	100	100	31	3642	0.68
4-methoxy	--	--	--	--	0.71
4-hydroxy	280	--	--	3620	0.56

1 oxidation of tetralin (23)

2 oxidation of petroleum (24)

3 reaction of α,α -diphenyl- β -picryl-hydrazyl (DPPH) with phenols (25)

4 infrared spectroscopy stretching frequencies of OH (cm^{-1})(26)

5 oxidation potential in volts (28)

IV. EXPERIMENTAL

EXPERIMENTAL

A. Polymerization Reactions

All reactions were carried out in ampoules constructed from 14 mm Pyrex tubing. These reaction vessels were 130 mm long and contained approximately 15 ml of reactants. The ampoules were thoroughly cleaned, rinsed with distilled water, and dried at 120°C before use. Solutions were introduced into the ampoules by means of volumetric pipettes and the ampoules were degassed at approximately 50 μ of Hg using two freeze-thaw cycles. Dry ice-acetone mixtures were used to solidify the solutions.

The sealed ampoules were immersed in a constant temperature oil bath equipped with a Scientific Industries submersion rotator (5-10 rpm) at 50.0 $\pm$.1°C. After the reaction had proceeded to about 10% conversion, the tubes were removed from the bath, cooled, and broken open. The polymer was precipitated from methanol in a Waring blender, separated by filtering the solution through preweighed Whatman #2 filter paper and dried in air at 45°C.

All solutions were prepared using standard volumetric techniques. The concentration of the initiator in all polymerization experiments was 1 mg/ml of monomer (6.1×10^{-3} M) and the concentrations of phenols ranged from 0.01 to 0.1 M.

B. Molecular Weight Measurements

The average degree of polymerization ($\bar{P}_n$) of the polymer samples was determined by dilute solution viscometry using a Fisher Scientific

viscometer of the Ubbelöhde type (2091, #1). Concentrations not greater than 0.5 g of polymer/100 ml of reagent grade benzene were used. Polymer and solvent in one ounce bottles were rotated end-over-end for at least three days to insure complete solution of the polymer.

Limiting viscosity values obtained by use of the equation presented in the previous section (Equation 16) were converted to number average $\bar{P}_n$ values by use of the following equation (30):

$$(17) \quad \log \bar{P}_n = 3.420 + 1.13 \log [\eta]$$

S. H. Pinner (31) has estimated that the error in the values of the limiting viscosity measurements due to the neglect of the kinetic energy term, to the error in timing, and to the neglect of densities may be as much as 2%. The kinetic energy term must be considered since flow-times are used instead of viscosity ratios. Assuming that another 3% error was introduced in the preparation of solutions and by the fluctuation of temperature, the combined error in the value of the limiting viscosity number may be as large as 5%. Since the limiting viscosity numbers obtained in this study ranged from 1.80 to 2.50, the values obtained should be within ± 0.01 .

The Mayo equation was used to determine the chain transfer constants. The other significant parameter which was the ratio of the concentrations of additive and monomer did not introduce a significant error. Since in some cases apparent transfer constants were evaluated, an error of up to 10% in the chain transfer constant values

could be tolerated in this study. Thus, the greatest error in the chain transfer constant determination results primarily from the evaluation of the limiting viscosity number and from the inadequacy of the Mayo equation in accounting for retardation effects. Some accuracy was sacrificed for convenience and practicality. Also, no adequate equation has been proposed to account for retardation effects.

C. Measurement of the Rate of Decomposition of the Initiator

The rates of decomposition of azobisisobutronitrile (AIBN) in the presence of several phenols were obtained by observing the nitrogen evolution at 81°C. This was of interest since the rate of polymerization of methyl methacrylate was faster in some phenols than in others. Solutions of xylene 0.10 M in initiator and 1.0 M in phenol were used. The total volume of the system was about 60 ml and the increase in volume due to the displacement of mercury in the manometer was 1.5 ml. A weighed amount of initiator was added to the xylene solution at 81°C in the reaction vessel, and the system was quickly closed. These solutions were stirred by a magnetic stirrer, and the reaction was allowed to proceed for 200 min. from the time of sealing.

Cm of Hg was plotted vs. reaction time and the pressure at infinite time (P_{∞}) was estimated. Since the half-life of the initiator at 80°C is around 75 min., a fairly good estimate of P_{∞} was obtained. The log of the value $P_{\infty} - \Delta P_t$ was plotted as a function of time using the estimated value of P_{∞} . ΔP_t is the difference in Hg levels of the manometer at a given time. The calculation method is shown in Part B of the Appendix.

The values of the rate constants could be estimated to ± 0.3 by use of this method. The values of the rate constants varied from 9.8 to $14.9 \times 10^{-3} \text{ min}^{-1}$. This indicates that error in the values was not less than 4%. The major sources of error in this technique arise from temperature fluctuations, the increase in volume due to the displacement of Hg in the manometer, and to the estimation of P_{∞} . Since an increase in volume of 2% due to the displacement of Hg in the manometer does not introduce significant error (32), the principal source of error is introduced by the other two parameters, the estimation of P_{∞} being the greater source of error.

D. Materials Used

Methyl methacrylate monomer obtained from Escambia Corporation and W. H. Curtin Chemical Company was purified by bulb to bulb distillation. The purified monomer was stored for periods of up to three weeks at -10°C without any polymer formation being observed.

The initiator, azobisisobutyronitrile (Vazo Du Pont, m. p. 102-103), was recrystallized from a benzene-toluene solution and stored in a dark bottle at room temperature.

All the phenols were readily available high purity materials except 4-isopropyl phenol which was obtained from the Alfred Bader Chemical Company. Since some of the phenols were oxidized very easily by air, they were stored at -10°C in a nitrogen atmosphere after purification. 2,6-di-*t*-butyl-4-methyl phenol was obtained from the Catalin Corporation (CAO-3).

V. EXPERIMENTAL RESULTS

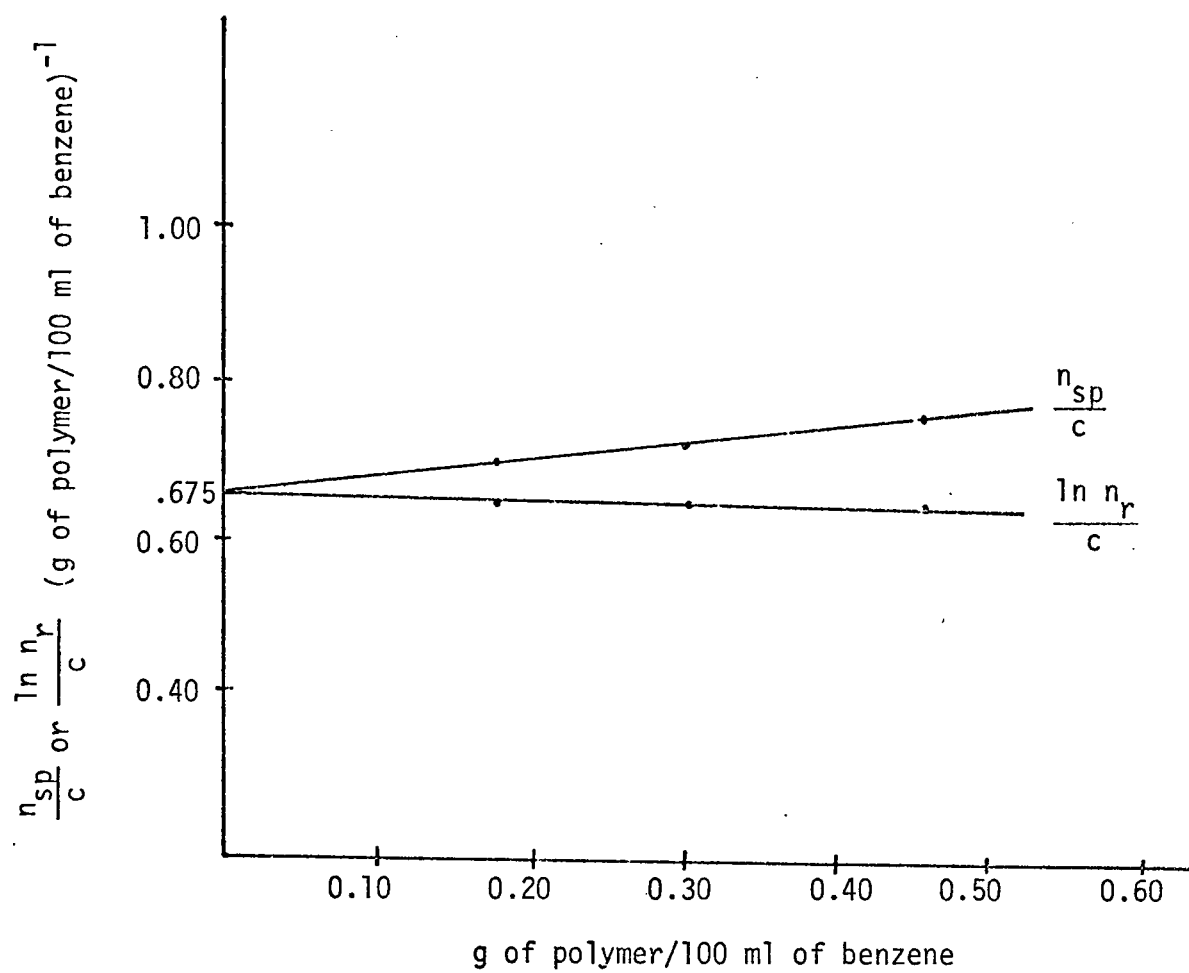
EXPERIMENTAL RESULTS

A. Checking Experimental Procedures and Techniques

1. Molecular Weights by Viscometry

The viscometry procedure was developed and standardized by use of a sample of polystyrene with a molecular weight of 97,000 which was obtained through the courtesy of the Dow Chemical Company. This sample was dissolved in chloroform, precipitated from methanol in a Waring blender, and dried. The flow times for polymer solutions were obtained with a capillary viscometer having a flow time of 130.7 sec for benzene at 24°C. Using flow times, the ratios η_{sp}/c and $\ln \eta_r/c$ were calculated as described previously and a limiting viscosity number $[\eta]$ of 0.675 was obtained from the intercept of a plot of these parameters vs. concentration (Figure 1). The limiting viscosity number (Equation 16) was determined as 0.678 by employing the η_{sp}/c and $\ln \eta_r/c$ ratios of the most concentrated solution. The actual limiting viscosity obtained by using the relationship $[\eta] = 9.55 \times 10^{-5} (9.7 \times 10^4)^{0.77}$ was 0.675. The constants for this equation were obtained by osmometry (33). The polystyrene sample used possessed a very narrow molecular weight distribution, i.e., the number average molecular weight ($\bar{M}_n$) and the viscosity average molecular weight ($\bar{M}_v$) were essentially equal. Thus, these preliminary experiments showed that this technique provided surprisingly good results.

FIGURE 1
DETERMINATION OF THE LIMITING VISCOSITY NUMBER $[\eta]$
OF A POLYSTYRENE SOLUTION (Mol. Wt. 97,000)



2. Molecular Weights by Gel Permeation Chromatography

The molecular weights and molecular weight distributions of poly(methyl methacrylate) samples were obtained by gel permeation chromatography (GPC) through the courtesy of the Dow Chemical Company. Methyl methacrylate was polymerized in the presence of phenol, 4-methylphenol, and 4-t-butylphenol. The concentration of the initiator was 6.1×10^{-3} M and that of the phenols was approximately 0.1 M. Limiting viscosity measurements gave $\bar{P}_n$ of 6.9, 6.2, and 6.6 (10^3), respectively. Figure 2 shows the molecular weight distributions obtained from the 1.5% solutions of these samples in tetrahydrofuran at room temperature. Since these curves are slightly skewed, the apex can not be taken as the molecular weight average. Nevertheless, this information indicates that the molecular weights obtained by viscosity measurements are very close to the ones obtained by GPC ($\bar{P}_n = 6-7 \times 10^3$). The chromatograms were obtained using columns of polystyrene beads (Dow's specifications) on a Waters GPC.

3. Evaluation of the Chain Transfer Constant of Cumene

The chain transfer constant of cumene with methyl methacrylate was calculated by the same technique used for phenols. Five solutions of different ratios of cumene to monomer were prepared and polymerized by techniques described previously. $\bar{P}_n$ values were obtained by the viscometry technique, using equation 16 to obtain the limiting viscosity number and equation 17 to convert the limiting viscosity number to $\bar{P}_n$. The slope of the line (Figure 3) is the chain transfer constant

FIGURE 2
MOLECULAR WEIGHT DISTRIBUTION CURVES (GPC) FOR
POLY(METHYL METHACRYLATE) SAMPLES POLYMERIZED
IN THE PRESENCE OF PHENOLS

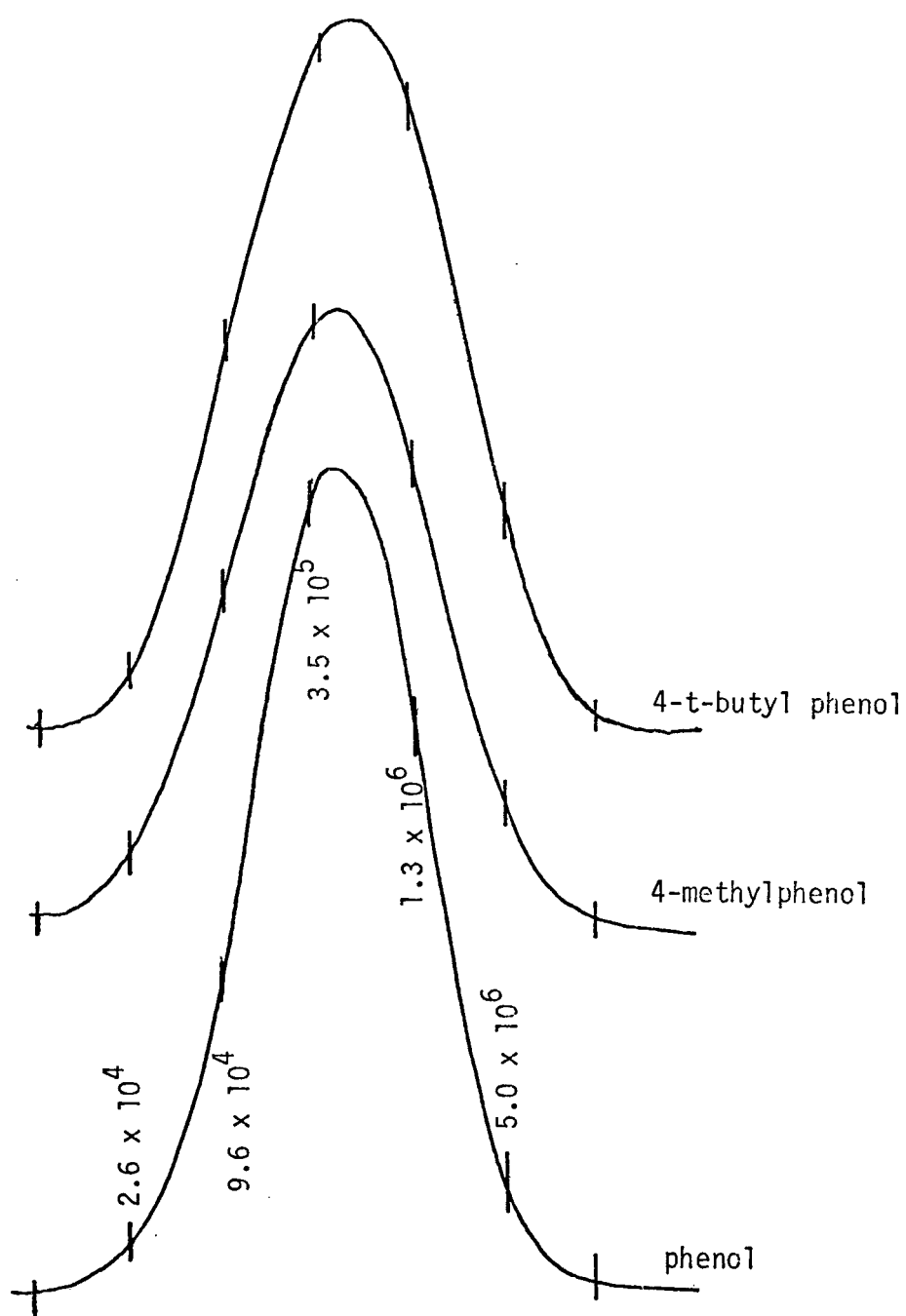
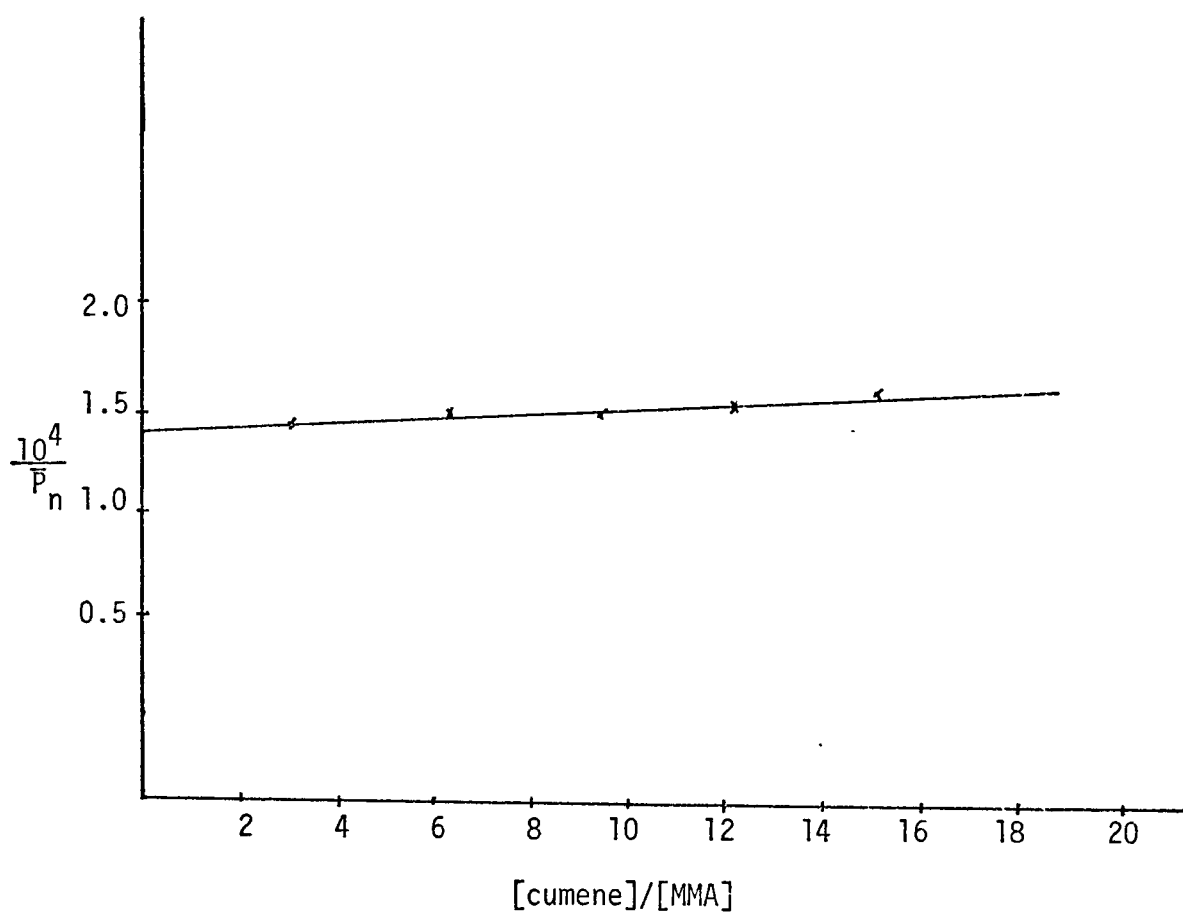


FIGURE 3
PLOT OF MAYO EQUATION FOR THE EVALUATION OF THE
CHAIN TRANSFER CONSTANT OF CUMENE WITH POLY(METHYL
METHACRYLATE) AT 50°C ($C_S = 1.10 \times 10^{-4}$)



($C_s = 1.10 \times 10^{-4}$) at 50.0°C, obtained from the Mayo equation. Chain transfer constants for cumene with this monomer have been obtained previously at 60 and 80°C. The values reported in the Polymer Handbook at 60°C are 2.56×10^{-4} and 1.9×10^{-4} . Those at 80°C are said to be less reliable and a value of 2.4×10^{-4} is given. These data indicate that the value calculated in this experiment at a lower temperature (50.0°C) is of the correct order of magnitude. This suggests that the techniques employed in this study are at least as reliable as those used by other investigators.

B. Chain Transfer Constants of Phenols

Plots of the Mayo equation for methyl methacrylate with several ortho alkyl phenols are shown in Figure 4. As shown in this figure, the chain transfer constant increases as the size of the substituent increases. These constants ranged from 2.5×10^{-4} for phenol to 24.4×10^{-4} for 2-sec-butylphenol. The inductive effect due to the electron-donating substituent was evaluated using para substituted phenols as shown in Figure 5. The values for the chain transfer constants of these compounds do not correlate well with the inductive effect of the substituents as will be shown later.

The chain transfer constants of compounds with groups other than alkyl groups are shown in Figure 6. Chain transfer constants for several di- and tri- substituted phenols are plotted in Figure 7. The values of the chain transfer constants for various phenols are summarized in Table II, and the method of calculation is shown in Part A of the Appendix.

TABLE II

CHAIN TRANSFER CONSTANTS AND EXTENT OF RETARDATION VALUES FOR
SUBSTITUTED PHENOLS AT 50°C WITH POLY(METHYL METHACRYLATE) RADICALS

Legend for Figures 4-15	Substituent	Chain transfer constants $\times 10^4$	Extent of Retardation*
a	none	2.5	.34
b	2-methyl	5.0	.75
c	2-ethyl	7.2	2.0
d	2-isopropyl	13.3	.85
e	2-t-butyl	21.4	1.9
f	2-sec-butyl	24.4	3.2
g	4-methyl	8.0	.37
h	4-ethyl	7.5	1.2
i	4-isopropyl	13.3	.70
j	4-t-butyl	9.5	.48
k	2-chloro	3.5	---
l	2-bromo	5.0	---
m	4-bromo	5.5	2.8
n	4-methoxy	8.0	2.6
o	4-cyano	6.0	.85
p	2,4-dimethyl	6.5	3.6
q	2,6-dimethyl	9.7	2.5
r	2,6-di-t-butyl	4.0	4.0
s	2,6-di-t-butyl- 4-methyl	5.5	9.0

*in g of polymer/mole of phenol/l of monomer

Figures 4-7 show that $(1/\bar{P}_n)_0$ varied in some experiments. This discrepancy may be due to an error in the concentration of the initiator, to impurities in the compounds, and to the effect of the phenol on the decomposition of the initiator. Also it was noted that at low monomer to polymer conversions $(1/\bar{P}_n)_0$ depended slightly on the pressure at which the ampoules were evacuated. Since the value of $(1/\bar{P}_n)_0$ is the sum of several chain transfer reactions (Equation 12), there is the possibility that in the presence of certain phenols other chain transfer reactions may be taking place at faster rates.

C. Extent of Retardation of the Polymerization Reaction

The extent of retardation of the polymerization of methyl methacrylate by phenols was conveniently measured by obtaining the polymer yields as a function of the phenol concentration. At least three solutions of varying concentrations of phenol and monomer in the presence of the initiator were polymerized at 50.0°C for 170 min. The ampoules were then removed from the bath, chilled, cracked open, and the contents were emptied into 50 ml Erlenmeyer flasks. Solutions were filtered through preweighed Whatman #2 paper and the polymer samples were allowed to dry overnight.

The polymer yield in the absence of phenols is shown in Figure 8 by the lone dot on the ordinate of the plot. On inspection, it is apparent that the curves do not have this point as their common intercept. Two experiments were performed to show that this was due to the difference in the efficiencies of these compounds as retarders and to

FIGURE 4
PLOT OF MAYO EQUATION FOR ORTHO ALKYL PHENOLS

(C_s values given in Table II, page 29)

- a - phenol
- b - 2-methyl phenol
- c - 2-ethyl phenol
- d - 2-isopropyl phenol
- e - 2-t-butyl phenol
- f - 2-sec-butyl phenol

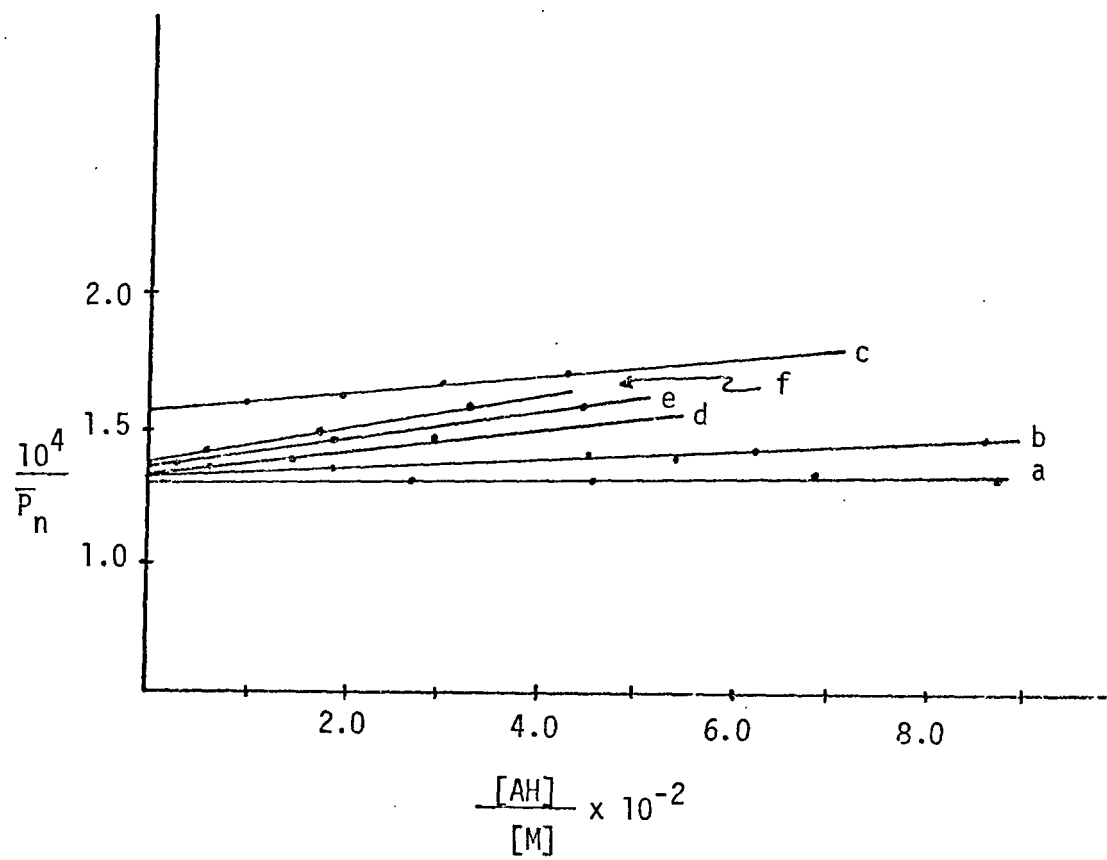


FIGURE 5
PLOT OF MAYO EQUATION FOR PARA ALKYL PHENOLS

(C_s values given in Table II, p. 29)

a - phenol

g - 4-methylphenol

h - 4-ethylphenol

i - 4-isopropylphenol

j - 4-t-butylphenol

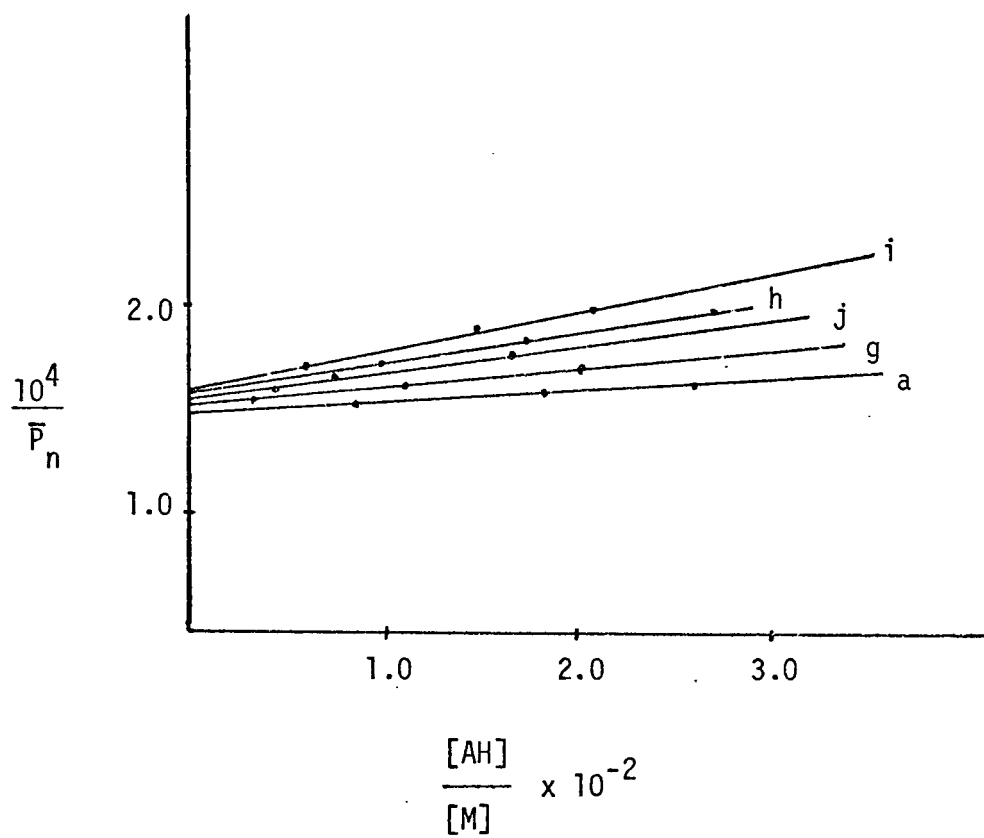


FIGURE 6
PLOT OF MAYO EQUATION FOR SOME ORTHO AND PARA NON-ALKYL PHENOLS
(C_s values given in Table II, p. 29)

k - 2-chlorophenol

l - 2-bromophenol

m - 4-bromophenol

n - 4-methoxyphenol

o - 4-cyanophenol

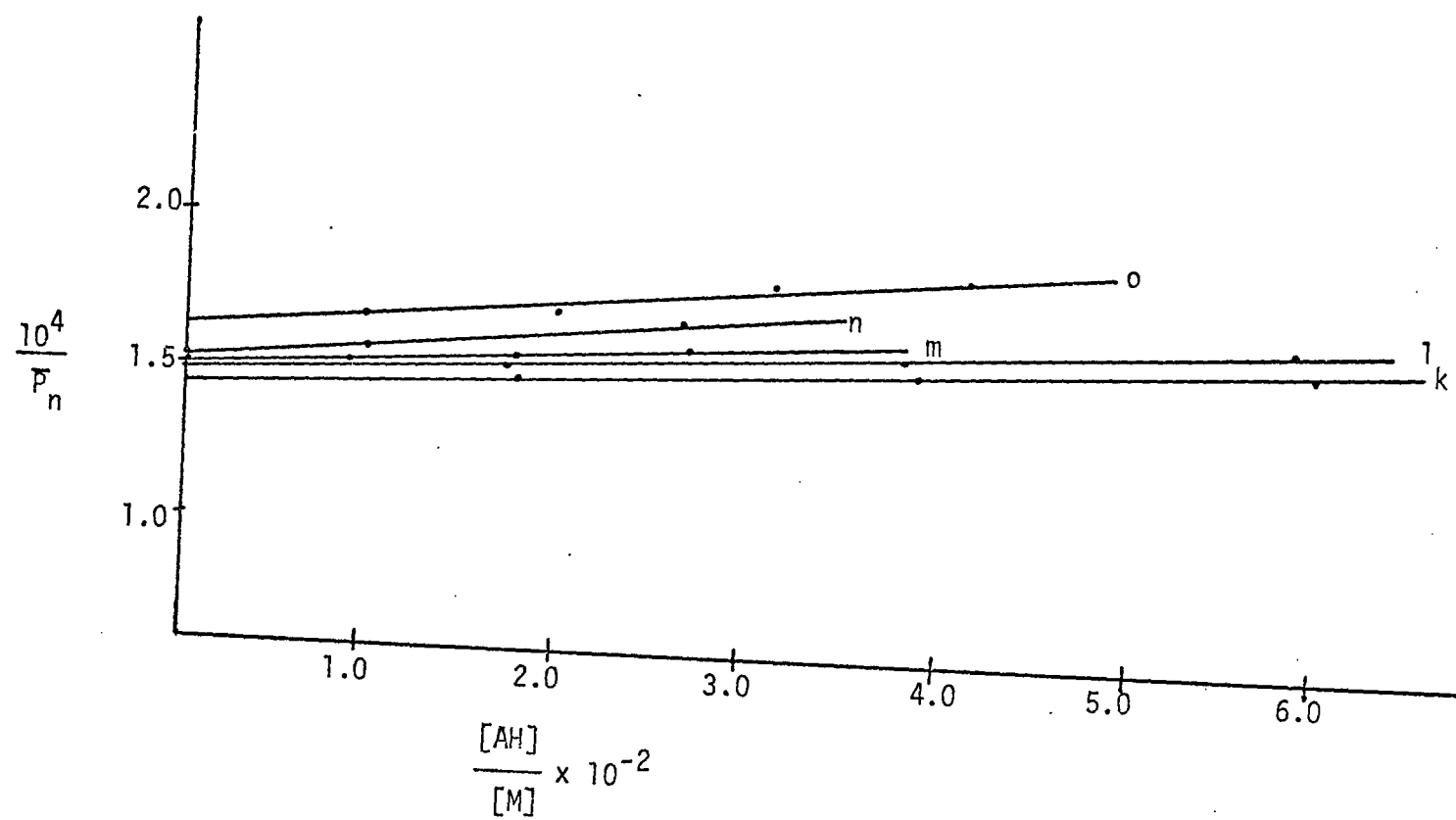


FIGURE 7
PLOT OF MAYO EQUATION FOR SOME DI- AND TRI- ALKYL PHENOLS

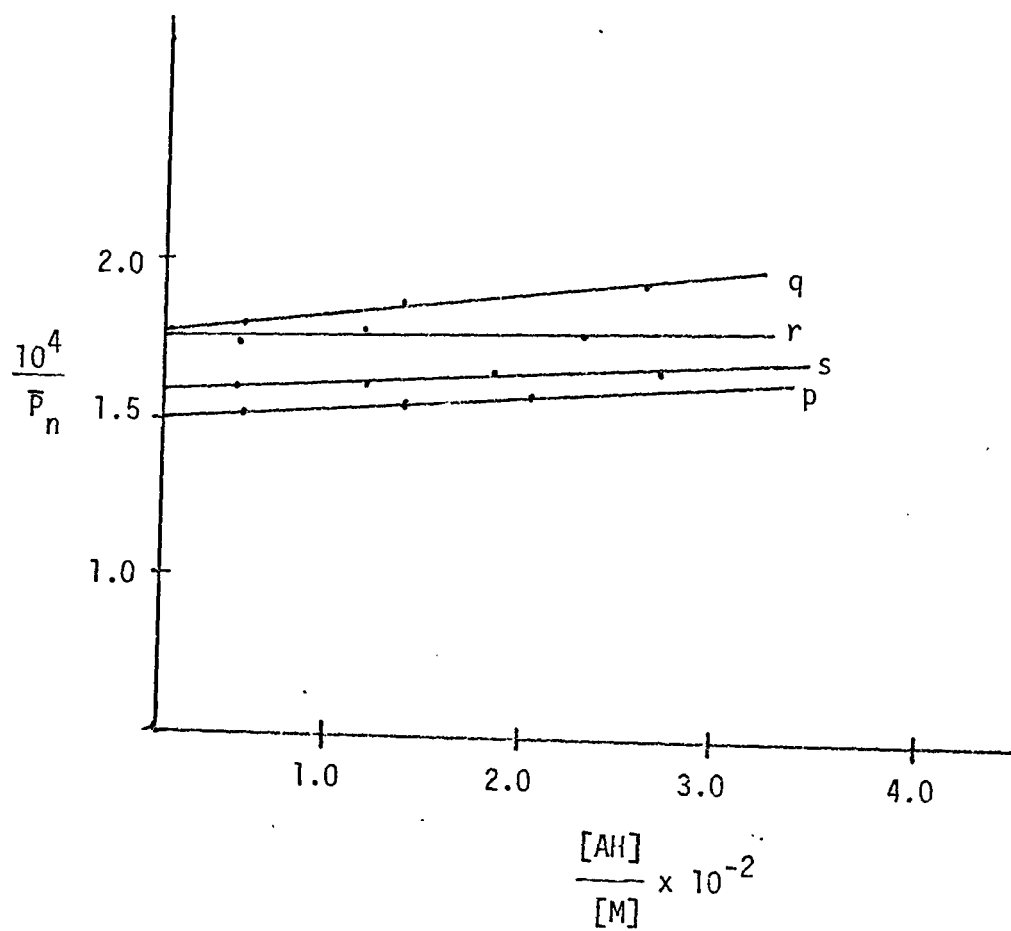
(C_s values given in Table II, p. 29)

p - 2,4-dimethylphenol

q - 2,6-dimethylphenol

r - 2,6-di-t-butylphenol

s - 2,6-di-t-butyl-4-methylphenol



an unexpected side reaction. Figures 8, 9, and 10 show the extent of retardation as measured by the above technique for several phenols.

D. Rate of Polymerization and Rate of Decomposition of the Initiator

Polymer yields (g) are plotted as a function of reaction time (min.) for solutions 0.25 M in phenols and 6.1×10^{-3} M in initiator (Figure 11). The intercepts on the abscissa indicate the retardation efficiencies of these compounds. If these compounds did not affect the rate of the decomposition of the initiator, the slopes of the lines should be approximately equal. However, since the slopes are different, it is apparent that the initiator is susceptible to side reactions.

Rates of decomposition of the initiator were measured by the evolution of nitrogen technique shown earlier. The results are tabulated in Table III along with rates of polymerization obtained from Figure 11.

A Hammett plot using σ values for the substituents and the data of Table III shows a good correlation between the σ values and the other parameters. A positive ρ value of 0.2 was obtained with both the rates of polymerization and the rate constants for the decomposition of the initiator (Figure 12). Contrary to previous reports (34,35), these results show that the initiator is susceptible to side reactions (36).

FIGURE 8
EXTENT OF RETARDATION (R_E) OF THE POLYMERIZATION
REACTION BY SOME PARA SUBSTITUTED PHENOLS

(R_E values given in Table II, p. 29)

- a - phenol
- g - 4-methylphenol
- h - 4-ethylphenol
- i - 4-isopropylphenol
- j - 4-t-butylphenol
- m - 4-bromophenol
- n - 4-methoxyphenol
- o - 4-cyanophenol

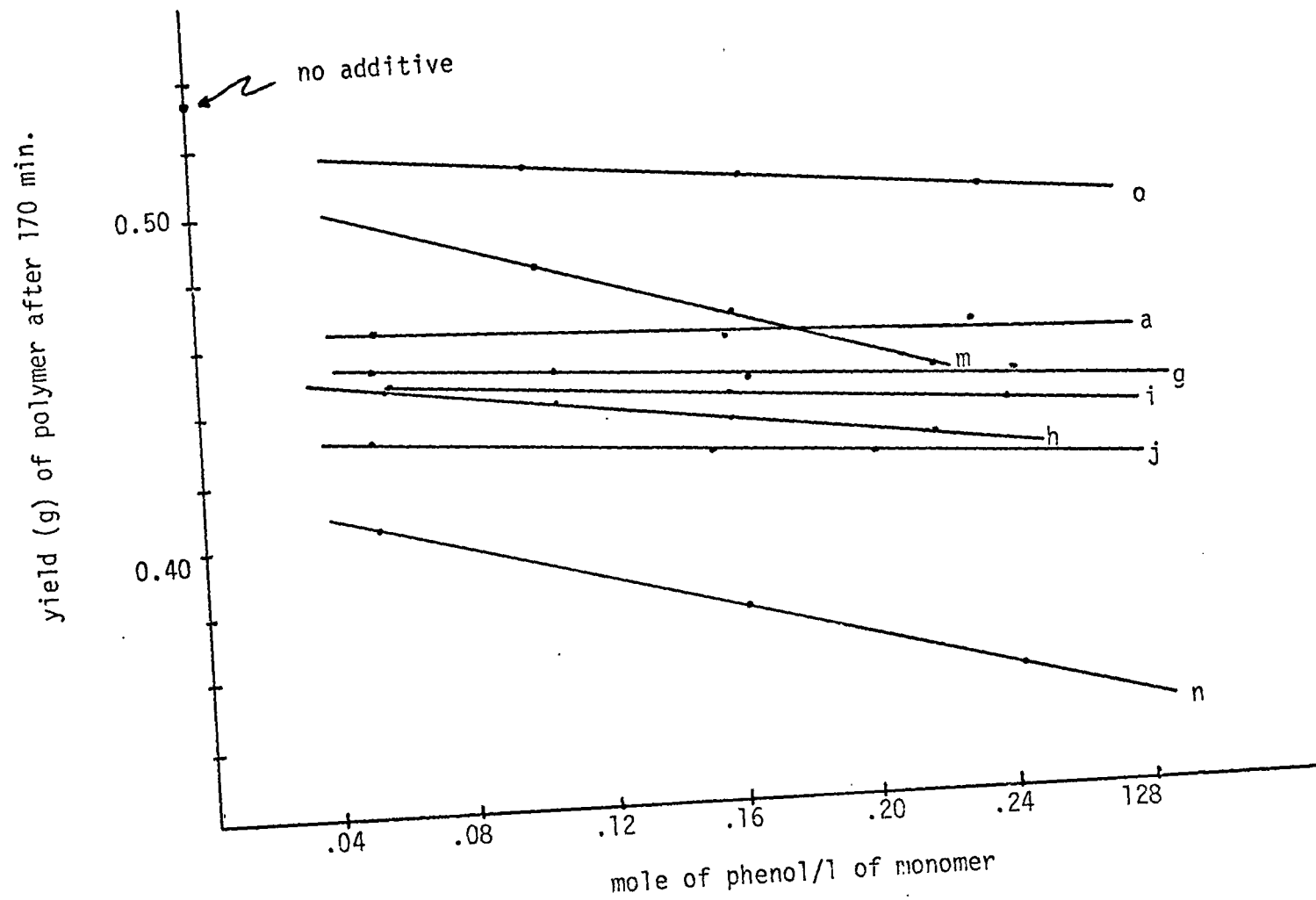


FIGURE 9
EXTENT OF RETARDATION OF THE POLYMERIZATION REACTION
BY SOME ORTHO ALKYL PHENOLS

(R_E values given in Table II, p. 29)

- b - 2-methylphenol
- c - 2-ethylphenol
- d - 2-isopropylphenol
- e - 2-t-butylphenol
- f - 2-sec-butylphenol

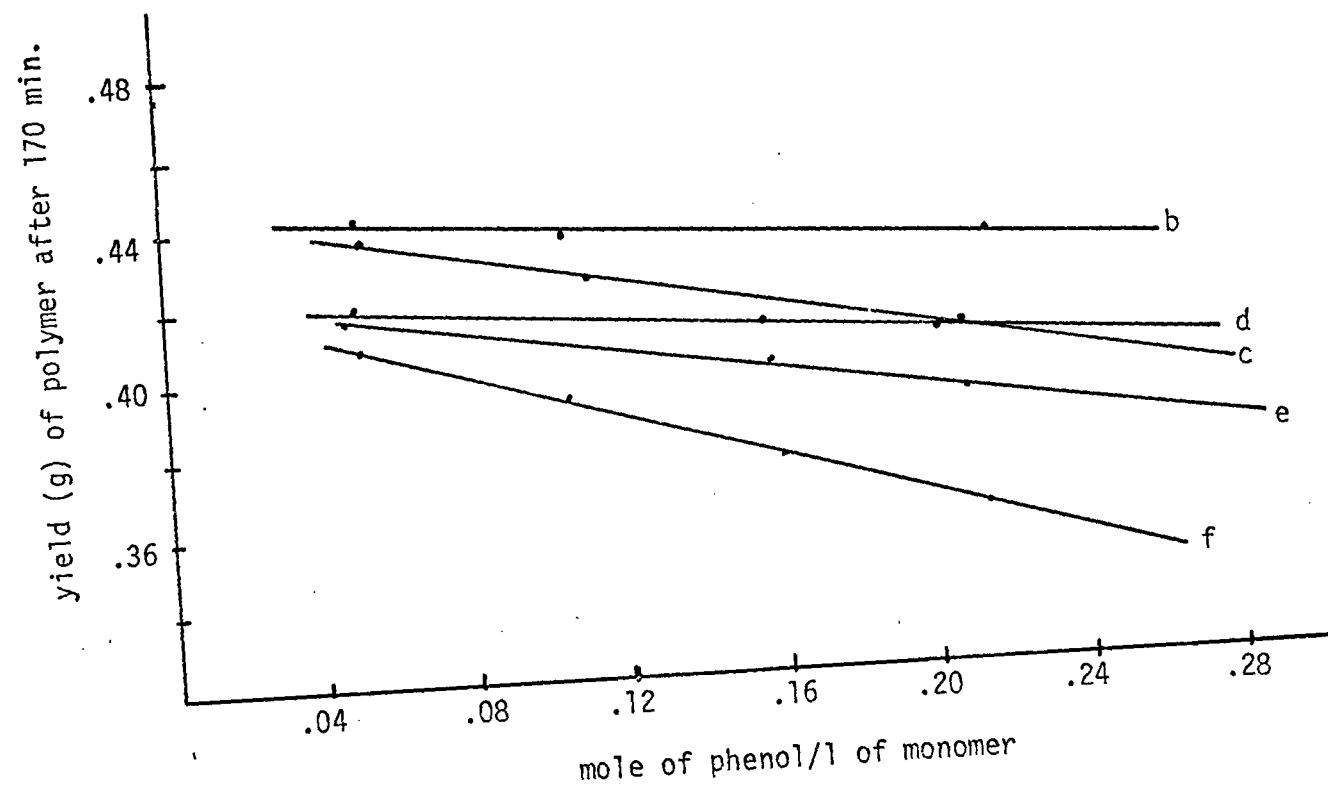


FIGURE 10
EXTENT OF RETARDATION ON THE POLYMERIZATION
REACTION BY DI- AND TRI- SUBSTITUTED PHENOLS

(R_E values given in Table II, p. 29)

p - 2,4-dimethylphenol

q - 2,6-dimethylphenol

r - 2,6-di-t-butylphenol

s - 2,6-di-t-butyl-4-methylphenol

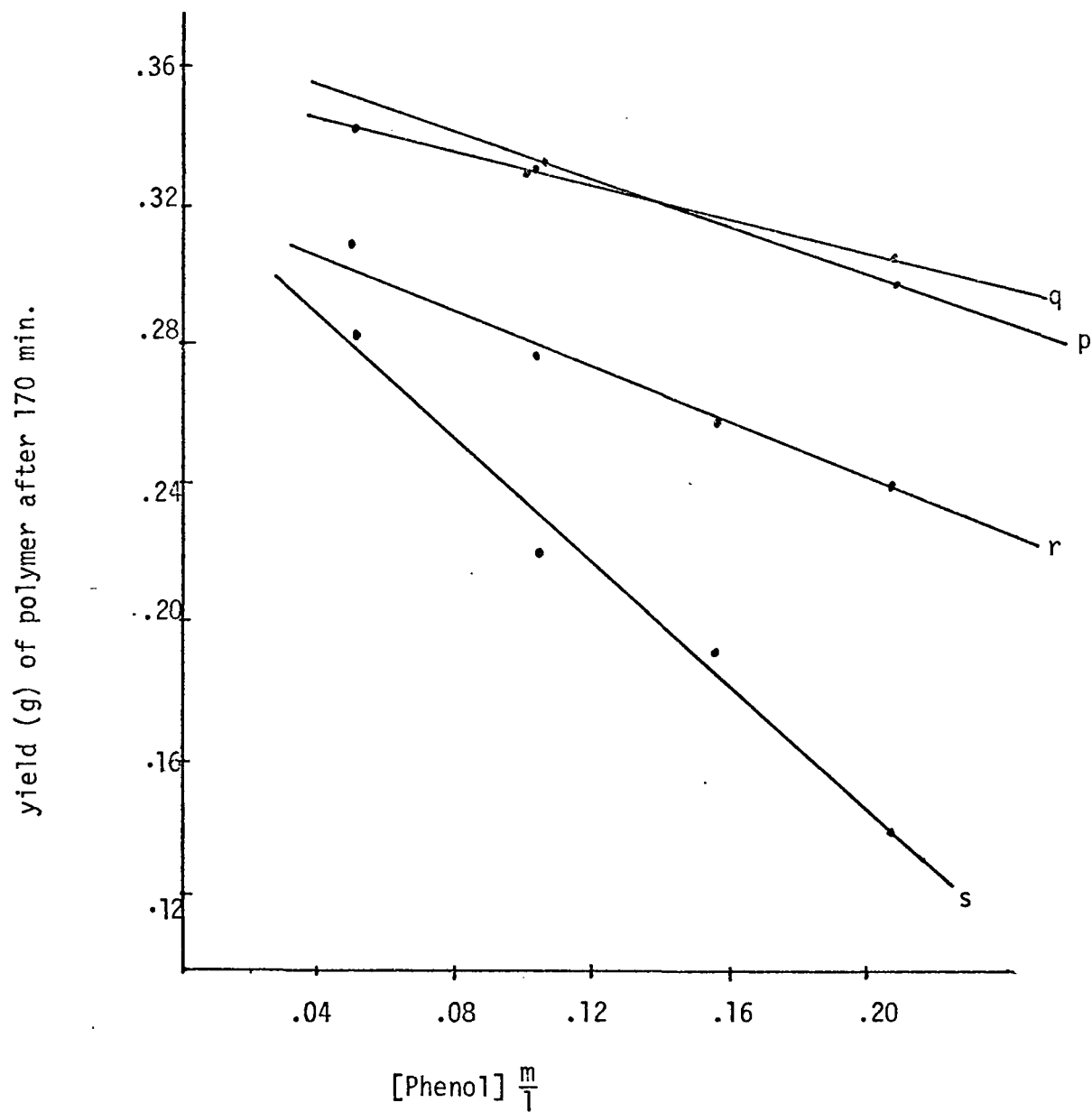


FIGURE 11
RATE OF POLYMER FORMATION IN THE PRESENCE
OF SEVERAL PHENOLS

n - 4-methoxy
e - 4-t-butyl
a - phenol
m - 4-bromo
o - 4-cyano
y - no additive

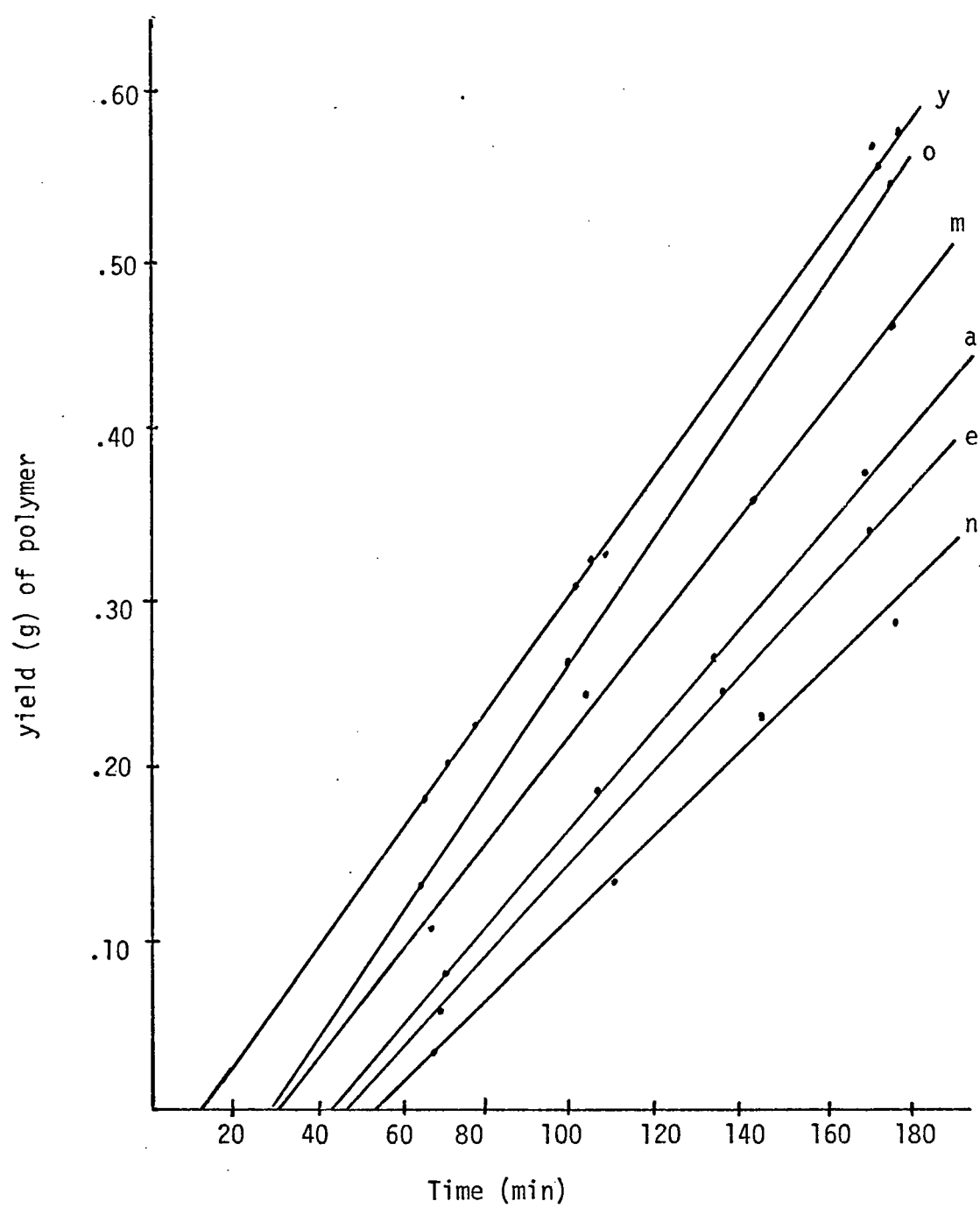


FIGURE 12
HAMMETT PLOT ($\rho = 0.2$) FOR THE RATE OF DECOMPOSITION
OF AIBN (x) AND RATE OF POLYMERIZATION OF METHYL METHACRYLATE (o)

n - 4-methoxyphenol

j - 4-t-butylphenol

a - phenol

m - 4-bromophenol

o - 4-cyanophenol

t - 4-nitrophenol

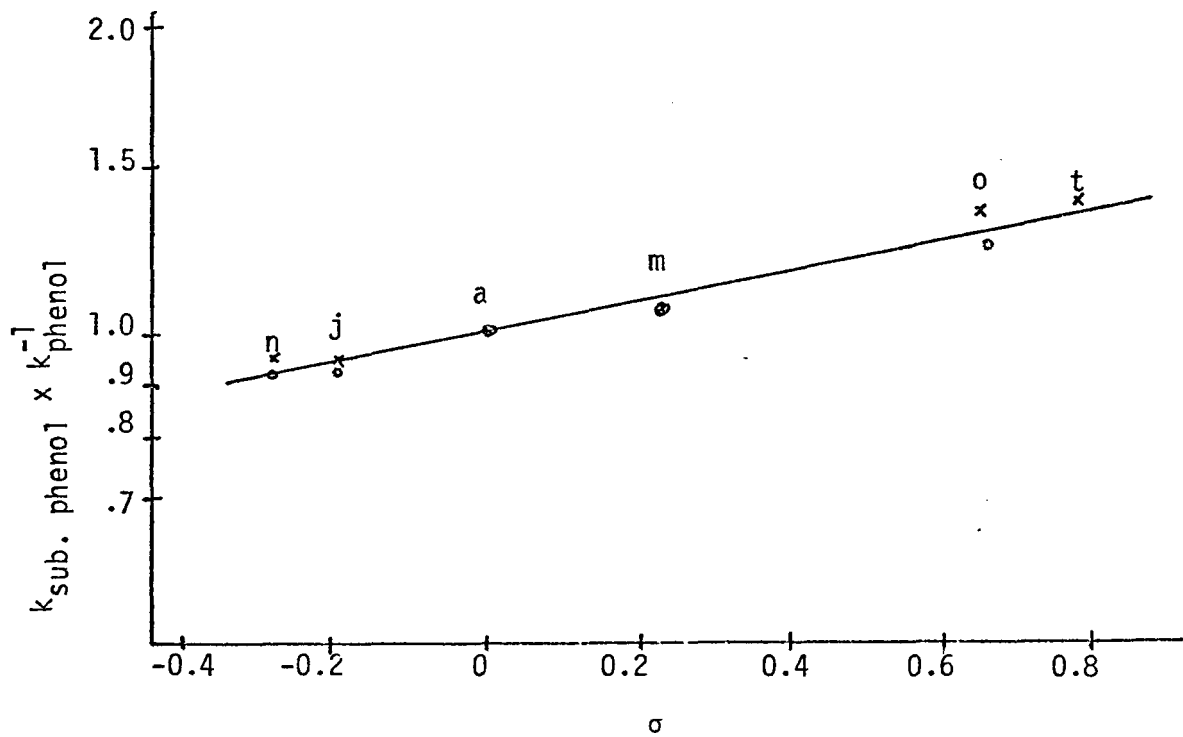


TABLE III
THE EFFECT OF PARA SUBSTITUTED PHENOLS ON THE
RATE OF DECOMPOSITION OF AIBN AND THE RATE OF
POLYMERIZATION OF METHYL METHACRYLATE

Substituent	Rate constants for decomposition of AIBN ($k_d \times 10^3 \text{ min}^{-1}$) plot legend (x)	Rate of polymerization of methyl methacrylate ($\text{g min}^{-1} \times 10^3$) plot legend (0)
t - nitro	14.9	---
o - cyano	14.6	3.76
m - bromo	11.1	3.18
a - none (phenol)	10.1	2.91
j - t-butyl	9.6	2.73
n - methoxy	9.8	2.50
y - control (no phenol)	10.5	3.41

V. DISCUSSION OF EXPERIMENTAL RESULTS

DISCUSSION OF EXPERIMENTAL RESULTS

A. Correlation of the Chain Transfer Constants with Antioxidant Efficiencies

Table IV presents in part the data from Tables I and II. It is apparent that a poor correlation is demonstrated when the chain transfer constants of the phenols obtained in this study are compared with the antioxidant ratings obtained by the other methods. The constants for the mono-substituted phenols indicate that the chain transfer constants increase as the size of the ortho substituents increase and as the electron donating ability of the groups increase. However, the effect is almost completely masked when two ortho groups sterically hinder the abstraction of the phenolic hydrogen. Thus, this method compares to that of the reactions of phenols with DPPH as shown in Column 3 of Table IV.

Another discrepancy is noted when the chain transfer constants for para substituted phenols are considered. In a previously mentioned study, Ingold showed that abstraction of phenolic hydrogens by t-butoxy radicals correlated well with Brown's σ^+ values. His study indicated that electron-donating groups facilitated the hydrogen abstraction reaction. When the chain transfer constants are correlated with σ values by means of a Hammett plot (Figure 13), a correlation such as observed by Ingold is not apparent. The chain transfer constants of para substituted phenols are always larger than that of phenol regardless of the nature of the substituents. A similar observation was made by Yamamoto and Otsu (37,38,39) who studied the reaction of substituted

TABLE IV
CORRELATION OF CHAIN TRANSFER CONSTANTS AND EXTENT OF RETARDATION
VALUES WITH ANTIOXIDANT RATINGS GIVEN BY OTHER METHODS

Substituent on phenol	I	II	III	IV	V	VI
none	4	1	4	0.92	2.5	0.34
2-methyl	26	14	47	0.85	5.0	0.75
4-methyl	15	10	55	0.84	8.0	0.37
2-t-butyl	53	24	---	0.81	21.4	1.9
4-t-butyl	23	7	83	0.84	8.8	0.48
2,4-dimethyl	55	47	789	0.76	6.5	3.6
2,6-dimethyl	56	32	117	0.76	9.7	2.5
2,6-di-t-butyl	49	---	---	0.68	4.0	4.0
2,6-di-t-butyl 4-methyl	100	100	31	0.68	5.5	9.0
4-methoxy	---	---	---	0.71	8.8	2.6
4-hydroxy	280	---	---	0.56	---	---

I oxidation of tetralin (23)

II oxidation of petroleum (24)

III reaction of DPPH with phenols ($1\text{-mole}^{-1}\text{ min}^{-1}$)(25)

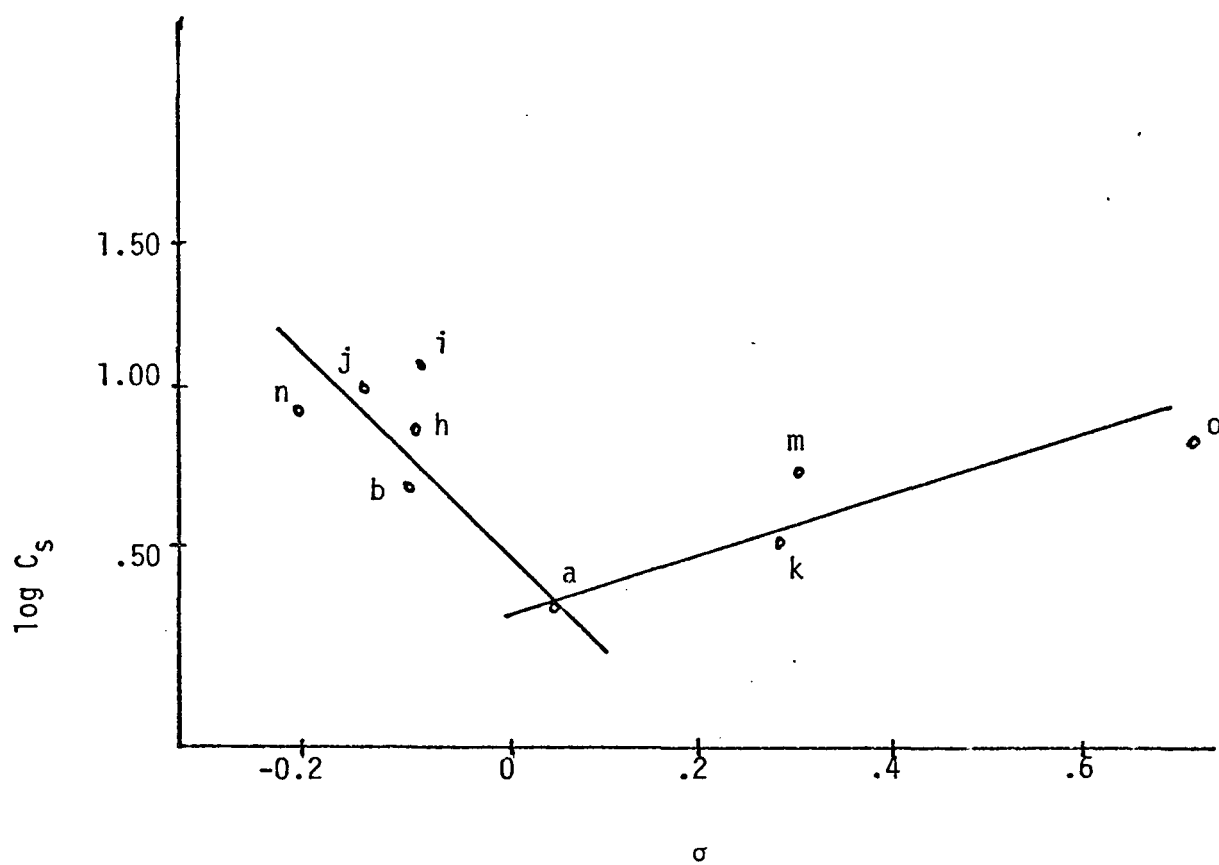
IV oxidation potential in volts (28)

V chain transfer constants (10^4) (this study)

VI extent of retardation of polymerization reaction in g of
polymer/mole of phenol/liter of monomer

FIGURE 13
HAMMETT PLOT OF CHAIN TRANSFER CONSTANTS (C_s) vs. σ

- a - phenol
- b - 2-methylphenol
- h - 4-ethylphenol
- i - 4-isopropylphenol
- j - 4-t-butylphenol
- k - 2-chlorophenol
- m - 4-bromophenol
- n - 4-methoxyphenol
- o - 4-cyanophenol

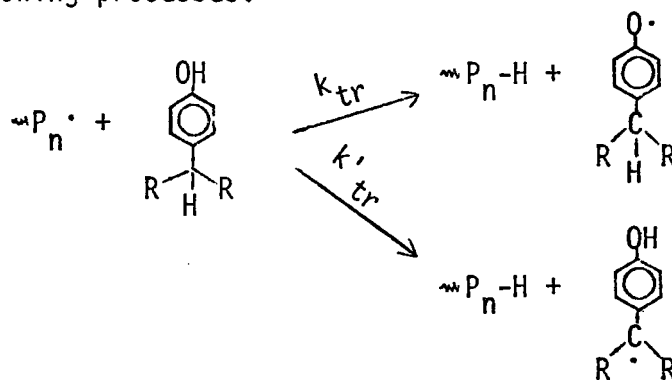


cumenes with poly(methyl methacrylate) and polystyrene radicals. These authors suggested that an additional parameter be incorporated in the Hammett equation to straighten the concave curve but did not comment on the nature of the discrepancy.

It is apparent that it is important to determine whether the correct ρ value is positive or negative, and why there is such a poor correlation among the alkyl groups. A number of previous studies have shown that Hammett correlations of the rates of free radical abstraction of hydrogen atoms with σ or σ^+ values have negative ρ values (40). Since the initiator, which is susceptible to side reactions, is the only other compound present in the reaction, the large values for the chain transfer constants for phenols with electron-withdrawing groups could be attributable to the interaction between the phenols and the initiator. However, it should be noted that methyl methacrylate does not polymerize readily in the absence of an initiator [about 1% yield of polymer is obtained at 60°C after 600 hours (41,42)]. Thus, the uncatalyzed reactions could not be carried out to investigate this suggestion further.

On the other hand, if the correct ρ value is positive, the explanation would be simpler but this would suggest that this reaction was unlike other known free radical reactions. A positive ρ value and the poor correlation among the alkyl substituents is in accord with the values of the chain transfer constants. As shown in Figure 5, the chain transfer constants increase as the ease of abstraction of the benzylic hydrogen increases. Furthermore, the small values of the

chain transfer indicate that the reaction of phenolic hydrogens with poly(methyl methacrylate) radicals is rather sluggish. This observation, which is in conflict with the isotopic effect observed by Ingold and others, could be explained by assuming that the growing polymer radicals abstract benzylic and phenolic hydrogen atoms at comparable rates. The fact that the bond strengths of $\text{O}-\text{H}$ and $\text{O}-\text{C}(\text{R})_2\text{H}$ are not very different and that the stabilities of the resultant benzylic and phenolic radicals are also comparable is in accord with this explanation. The abstraction of hydrogen atoms other than phenolic hydrogen atoms would give a chain transfer constant that was a summation of the ratios of the following processes.



$$C_s = \frac{k_{tr} + k'_{tr}}{k_p}$$

If as suggested, the poly(methyl methacrylate) radicals abstract hydrogen atoms at random, then phenols with alkyl substituents would always have larger chain transfer constants than phenol. That the sum of the chain transfer constants of phenol (2.5×10^{-4}) plus that of isopropyl benzene (1.1×10^{-4}) indicates that this value (3.6×10^{-4}) was less than that of 4-isopropyl phenol (13.3×10^{-4}) was

pointed out by B. J. Yager (43). However, the sum of the individual chain transfer constants alone does not account for the effect of the substituent on the abstraction reaction in the phenol molecule. Also, the chain transfer constants of 4-*t*-butyl phenol and 4-methoxyphenol which lack benzylic hydrogens are larger than that of phenol. Unfortunately, the further experimentation which is essential to answer these questions is beyond the scope of the present study.

B. Correlations of the Extent of Retardation with Chain Transfer Constants and Antioxidant Activities

It is evident that chain transfer constants in Table IV do not correlate well with retardation values. Yet, the data in Table IV and Figure 14 show a good correlation between retardation values and antioxidant efficiencies as measured by the oxidation of petroleum (Column 2, Table IV). Attempts to correlate these values with antioxidant ratings obtained from the oxidation of tetralin (Column 1, Table IV) and with the oxidation potentials of phenols (Column 4, Table IV) were not as successful.

Data on Figure 11 suggest that retardation of polymerization appears to be due to the action of oxygen and the phenols since inhibition times were proportional to the amount of oxygen present and the activity of the phenols. The inhibition time for 4-methoxyphenol was the longest. This is in accord with Ingold's observation that electron-donating groups increased the efficiency of phenols. A plot of σ values vs. inhibition times obtained from the intercepts on the abscissa of Figure 11 is shown in Figure 15.

FIGURE 14
CORRELATION OF EXTENT OF RETARDATION VALUES WITH
ANTIOXIDANT RATINGS OBTAINED FROM THE OXIDATION
OF PETROLEUM (22).

- a - phenol
- b - 2-methylphenol
- e - 2-t-butylphenol
- g - 4-methylphenol
- j - 4-t-butylphenol
- p - 2,4-dimethylphenol
- q - 2,6-dimethylphenol
- s - 2,6-di-t-butyl-4-methylphenol

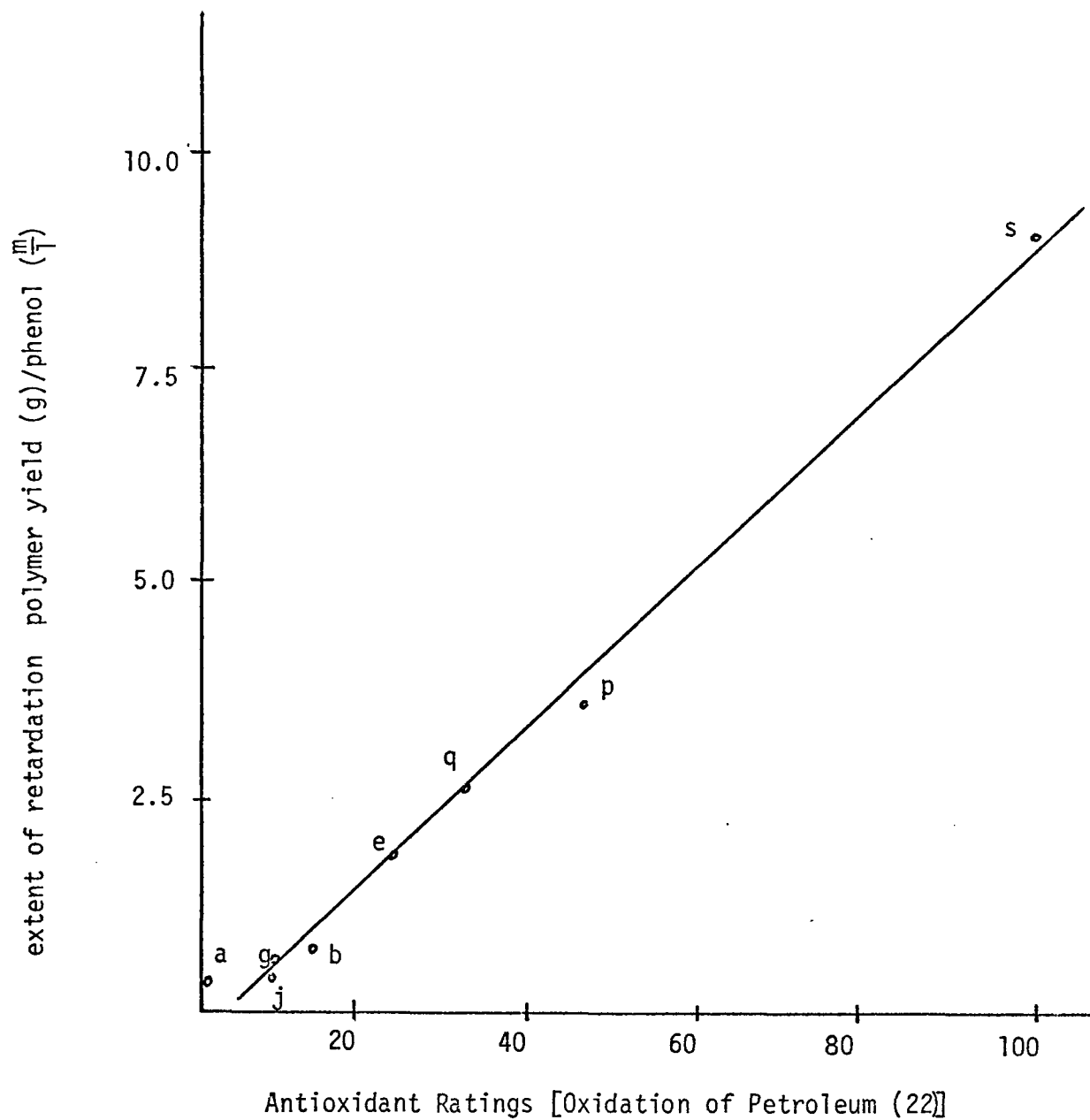


FIGURE 15
HAMMETT PLOT OF INHIBITION TIMES VS. σ VALUES.
INHIBITION TIMES OBTAINED FROM FIGURE 11.

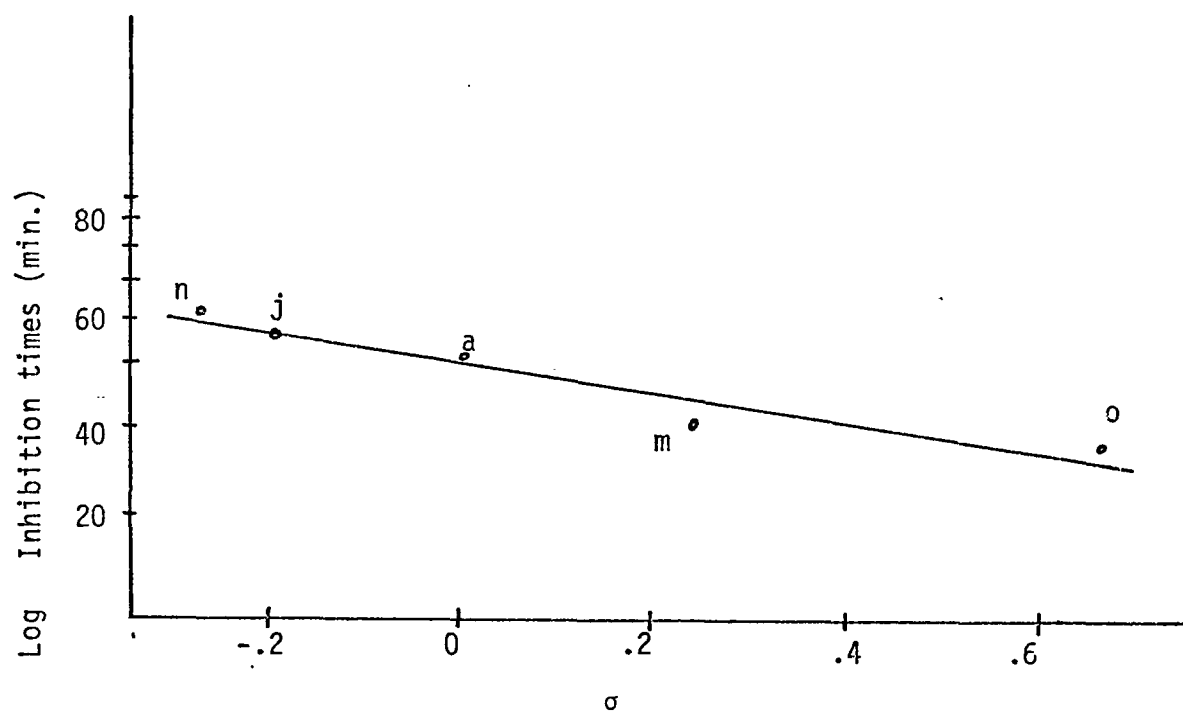
n - 4-methoxyphenol

j - 4-t-butylphenol

a - phenol

m - 4-bromophenol

o - 4-cyanophenol



Presumably the polymerization proceeds as soon as the oxygen in the system is consumed and the phenols act as very poor retarders. This specific retardation effect is masked by the effect of phenols on the decomposition of the initiator. This unexpected side reaction prevented the obtaining of information on the relative stabilities of the phenoxy radicals.

C. Suggestions for Further Investigations

Although a correlation of chain transfer constants and antioxidant efficiencies was not demonstrated, little information on the relative labilities of phenolic hydrogen atoms was obtained, and no information on the stabilities of phenoxy radicals was provided, this study (44) did reveal areas for further investigation to provide the desired information on the relationship between chemical structure and antioxidant efficiencies.

Suggestions for further investigations are as follows:

1. Since ortho disubstituted phenols hinder the attack of the OH group by bulky radicals, a system such as ethylene or ethylene oxide that provides propagating species that are not bulky should be considered.
2. Reactions that yield lower molecular weight products are necessary so that the end products can be analyzed by conventional instrumental methods. This is essential to determine the fate of the phenoxy radical in these reactions. Also characterization of the oligomers produced in these reactions would

reveal whether free phenolic groups were present. This, in turn, would show whether hydrogen atoms from other groups in a molecule are also abstracted.

3. Reactions thermally initiated should also be considered since side reactions that mask the important reaction can occur as demonstrated in this study.
4. The method used to obtain extent of retardation values should be investigated in other monomer systems to see if it is really a better and more convenient test method than those already being used.

VII. CONCLUSIONS

CONCLUSIONS

This study revealed the following:

1. Chain transfer constants do not correlate with antioxidant efficiencies, possibly because the growing polymer radical is too bulky and can not readily abstract phenolic hydrogen atoms from hindered phenols.
2. The extent of retardation of the polymerization of methyl methacrylate by phenols yields information that correlates chemical structure with antioxidant efficiencies obtained from the oxidation of petroleum.
3. Chain transfer constants of phenols do not correlate with the extent of the polymerization reaction, presumably because of the small amount of oxygen present even though reactions were carried out at 50-75 μ of Hg.
4. The method used to evaluate the extent of retardation can be used to correlate antioxidant efficiencies with chemical structure provided that the effect of the antioxidant of the initiator is known.
5. Phenolic hydrogen atoms may be abstracted at comparable rates to benzylic hydrogens in a system where the attacking radical is sluggish in reacting with phenolic hydrogens.
6. Contrary to previous reports, the initiator, azobisisobutyronitrile, is susceptible to side reactions.

7. Inhibition times correlate well with Hammett σ values with a negative ρ value, but chain transfer constants do not correlate well with the same Hammett parameter.

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APPENDIX

PART A. EVALUATION OF THE CHAIN TRANSFER CONSTANT OF PHENOL

1. Evaluation of $[AH]/[M]$.

Solution Number	g. of phenol per 5 ml. of monomer	mole of phenol (10^4)	$\frac{[AH]^*}{[M]} \times 10^2$
2	.0816	8.70	1.84
3	.1224	13.0	2.76
4	.1632	17.3	3.46
5	.0408	4.35	1.16 ¹
6	.0816	8.70	1.84
7	.1224	13.0	2.76
9	.1224	13.0	4.60 ²
10	---	---	---

* 5 ml. of MMA = 4.71×10^{-2} mole

1 MMA = 3.77×10^{-2} mole

2 MMA = 2.83×10^{-2} mole

2. Evaluation of $[\eta]$ (Equation 16).

Solution Number	I	II	III	IV	V	VI	VII	VIII
2	.495	192.8	2.64	1.64	.838	.970	1.47	2.31
3	.466	182.7	2.51	1.51	.810	.920	1.48	2.29
4	.452	178.8	2.45	1.45	.804	.895	1.48	2.28
5	.487	190.7	2.61	1.61	.825	.959	1.47	2.30
6	.473	189.1	2.59	1.59	.840	.952	1.51	2.35
7	.501	192.5	2.64	1.64	.870	.970	1.45	2.27
9	.490	187.9	2.57	1.57	.801	.944	1.44	2.24
10	.495	211.6	2.76	1.76	.880	1.015	1.54	2.43

I $c = \text{g of polymer/100 ml of benzene}$

II flow rate (sec) (flow rate for benzene = 73.0 sec at 25.0°C)

III $t/t_0 = n_r$ ($t_0 = \text{flow time for benzene}$) ($t = \text{flow time for solution}$)

IV $n_r - 1 = n_{sp}$

V $n_{sp}/4c$

VI $\ln n_r$

VII $3 \ln n_r/4c$

VIII $n_{sp}/4c + 3 \ln n_r/4c = [\eta]$

3. Evaluation of $1/\bar{P}_n$ (Equation 17).

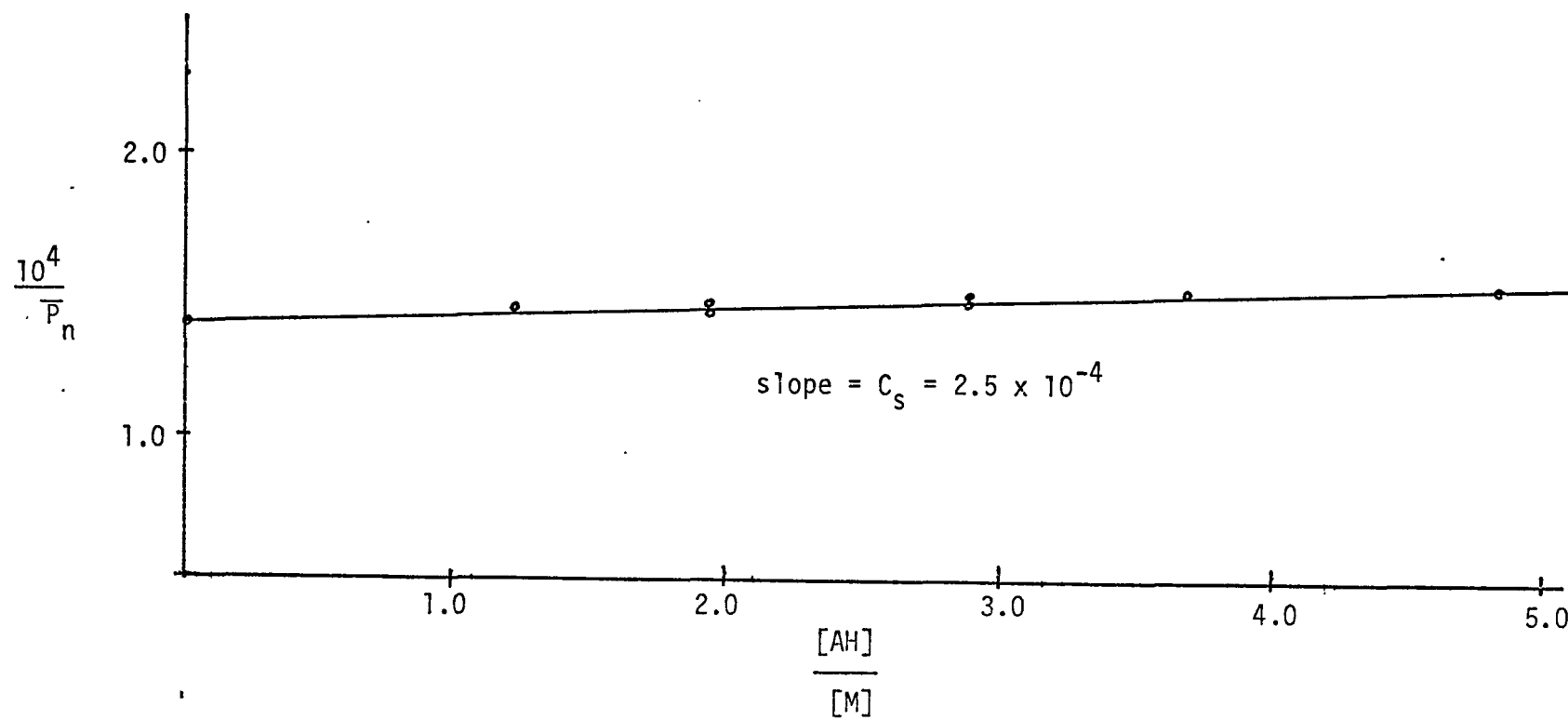
Solution Number	I	II	III	IV
2	.411	3.831	6.77	1.48
3	.407	3.827	6.70	1.49
4	.405	3.825	6.67	1.50
5	.410	3.830	6.75	1.48
6	.419	3.839	6.80	1.45
7	.403	3.823	6.65	1.51
9	.396	3.816	6.54	1.52
10	.435	4.855	7.15	1.40

$$\text{I } 1.13 \log [n]$$

$$\text{II } 1.13 \log [n] + 3.420$$

$$\text{III } \bar{P}_n \times 10^{-3}$$

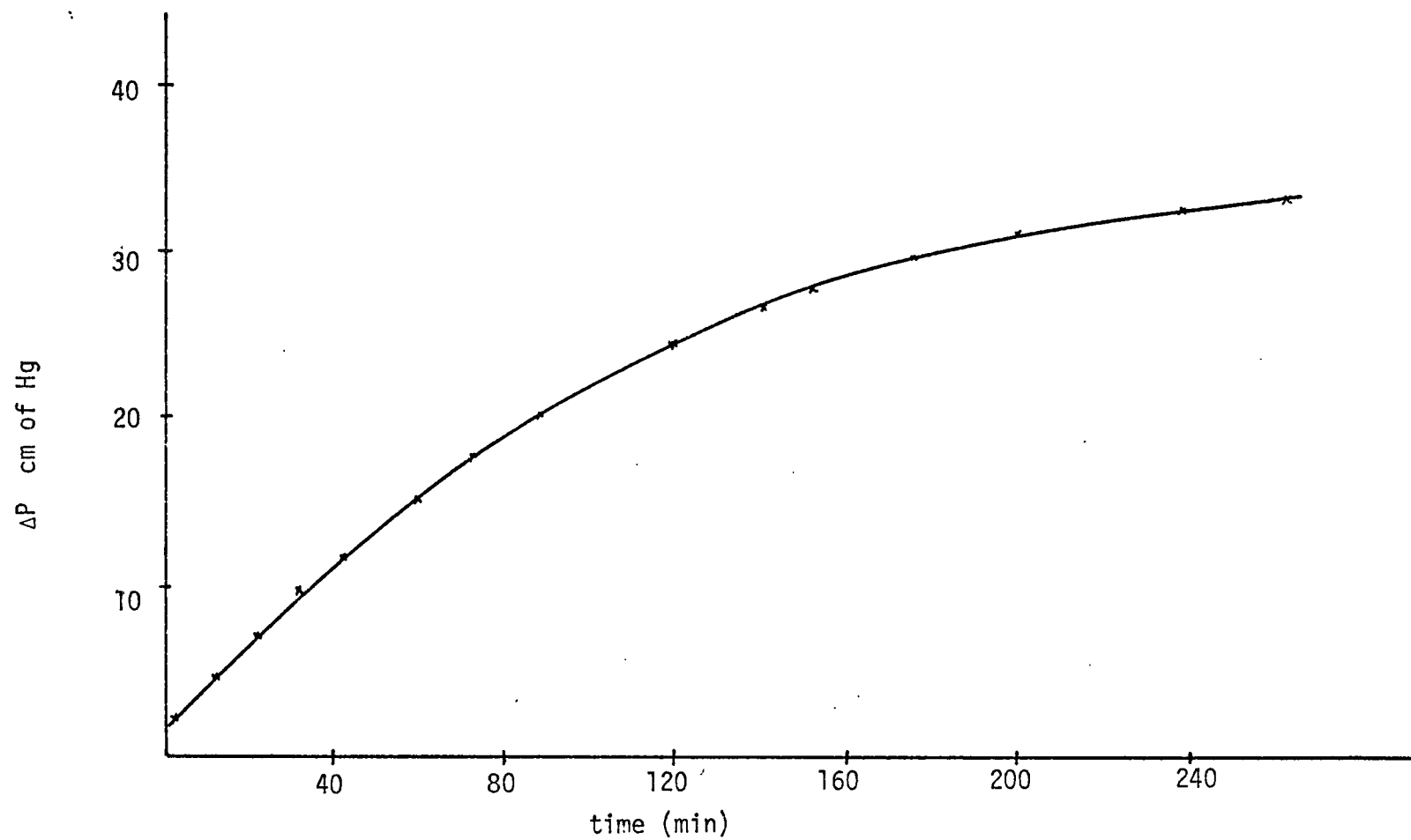
$$\text{IV } 10^4/\bar{P}_n$$



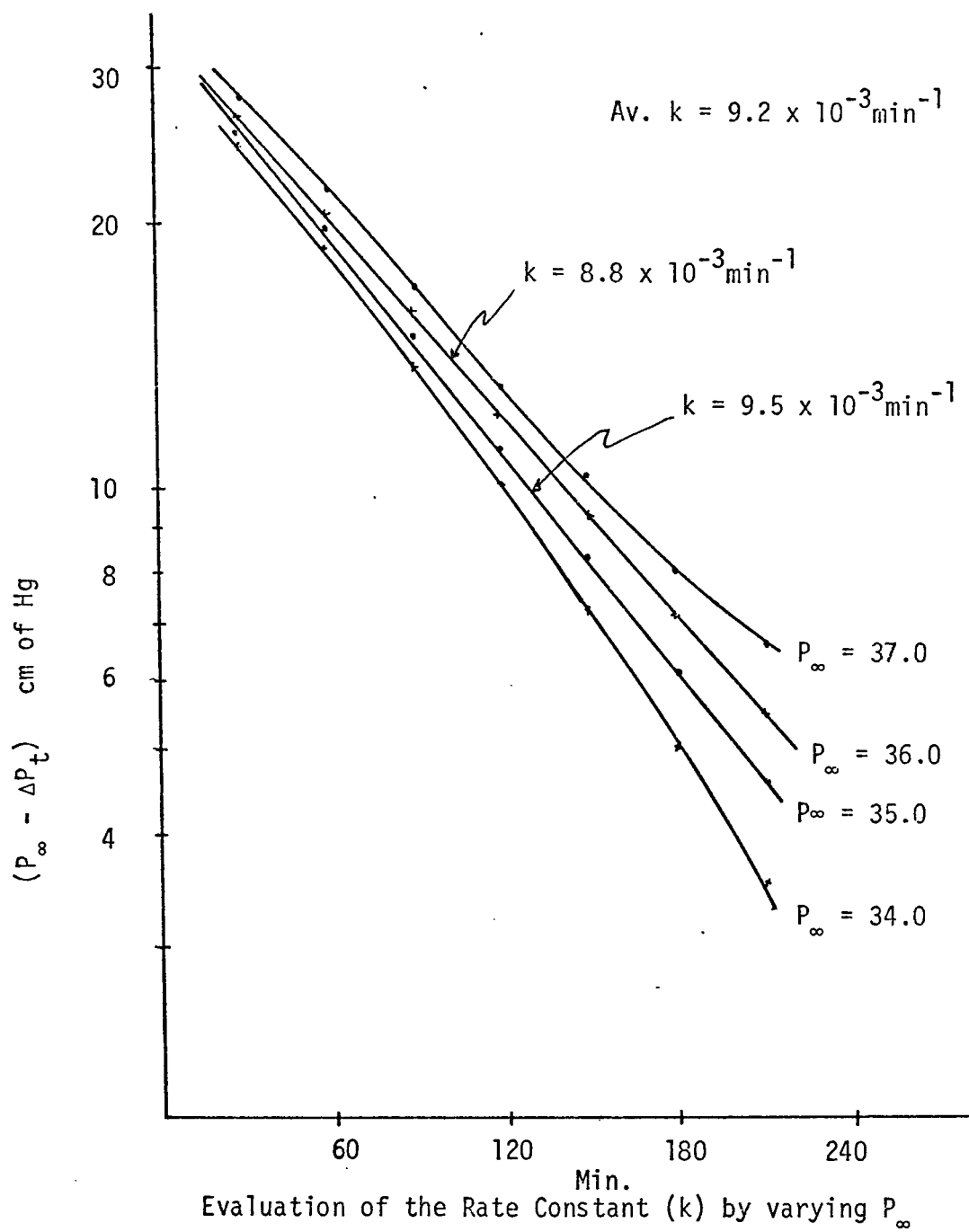
Chain Transfer Constant for Phenol Using Data Given in Part A.

PART B. DATA FOR THE EVALUATION OF THE RATE CONSTANT OF AZOBISISO-BUTYRONITRILE (0.15 g) IN THE PRESENCE OF 4-METHOXY PHENOL (0.6 g) IN 10 ml OF XYLENE

Time	Extent of Reaction (min)	Temp °C	Reading of manometer cm of Hg	Difference ΔP in cm
9:00	0.0	81.0	---	---
9:01	1.0	81.0	33.2 31.3	1.7
9:10	10.0	81.0	34.5 30.1	4.4
9:20	20.0	80.9	35.8 28.8	7.0
9:30	30.0	80.9	37.1 27.5	9.6
9:40	40.0	80.9	38.2 26.5	11.7
9:58	58.0	80.8	39.9 24.7	15.2
10:11	71.0	80.7	41.1 23.6	17.5
10:27	87.0	80.7	42.3 22.4	19.9
10:58	118.0	80.8	44.2 20.5	23.7
11:19	139.0	80.9	45.3 19.5	25.8
11:30	150.0	81.0	45.7 19.0	26.7
11:55	175.0	81.0	46.7 18.0	28.7
12:19	199.0	81.1	47.4 17.3	30.1
12:57	237.0	81.2	48.1 16.7	31.4
1:19	259.0	81.0	48.3 16.5	31.8



Plot of Increase in Pressure Due to the Evolution of Nitrogen vs. Time



PART C. DISCUSSION OF THE LIMITATIONS OF THE MAYO EQUATION

Two assumptions inherent in the derivation of the Mayo equation are that the additive must not retard the polymerization reaction and that other chain transfer reactions must be at a minimum.

Retardation of polymerization may occur when oxygen or other reactive impurities are present or when a chain transfer agent produces a resultant radical that is unable to initiate a new chain. When oxygen or other reactive impurities are present, the reaction is inhibited until any inhibitors are consumed. The reaction then proceeds at its normal rate. When an additive that retards the polymerization is present, the polymerization reaction proceeds at a lower rate throughout.

If reactive impurities are present and if the inhibition time is small, then chain transfer constants calculated by the Mayo equation should be unaffected since the extent of polymerization is allowed to proceed to approximately 10 percent and any undesired low molecular weight by-products formed do not effect the molecular weight distribution significantly. In contrast, if the inhibition period is long and the extent of polymerization is less than 10 percent, the effect of the low molecular weight by-products would be more significant. Chain transfer constants are still considered to be accurate, if less than 5 percent retardation occurs. When greater than 5 percent retardation occurs, different forms of the Mayo equation must be used.

The other assumption mentioned requires that other chain transfer reactions remain at a constant minimum. Occasionally, side reactions are observed when an initiator such as benzoyl peroxide is used since solvents affect the rate of decomposition of this initiator. Since this initiator is susceptible to a chain induced decomposition, it is not used in chain transfer studies.

When the Mayo equation is used to determine chain transfer constants, variations in $(1/\bar{P}_n)_0$ may be noted when one or more of these side reactions occur. The extent to which this variation affects the chain transfer constant depends on the complexity of the system studied.

The reactions between poly(methyl methacryl) radicals and phenols were investigated in the absence of oxygen. Although phenols are good inhibitors because of their low oxidation potentials, they are poor retarders in the absence of oxygen as indicated by their low chain transfer constants.

The variation of $(1/\bar{P}_n)_0$ in this study is due to the difference in the rate of decomposition of the initiator and any retardation caused by residual oxygen and/or the phenols, as well as experimental error in the determination of the limiting viscosity number. As shown by Figure 11, page 39, the inhibition period is small and the retardation or the acceleration of the rate of polymerization is due to the effect of the phenols on the initiator. Thus, the retardation by simple phenols was masked by this side reaction. This premise is in accord with data in Figure 12, page 40, and Table III, page 41.

Furthermore, the molecular weights obtained by GPC are extremely high. These data suggest that any low molecular weight products formed during the short inhibition period do not contribute significantly to the molecular weight distribution.

The effect of the variation of $(1/\bar{P}_n)_0$ on the chain transfer constant is difficult to evaluate but the effect was not considered to be too significant in this study. The calculated constants increased as the size of the ortho groups increased for mono substituted compounds and decreased as the size of the ortho groups increased in disubstituted compounds. This effect is also demonstrated by the reactions of DPPH with phenols, which provide a qualitative measure of the hydrogen abstraction. Since chain transfer constants for this system are lower than those obtained for polystyrene and poly(vinyl acetate) radicals, constants calculated here are of the correct order of magnitude.

Thus, while the system studied was complex, it appears that the calculated chain transfer constants were sufficiently accurate to correlate with the rate constants for the reactions of DPPH with phenols. Furthermore, many of the constants evaluated are similar to those reported by other investigators.

Equations that include retardation effects usually give lower values than the apparent chain transfer constants calculated by use of the Mayo equation. Equations that take into consideration some of the factors mentioned above have not been developed because they would be too complicated.