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Problems in Radical Polymerizations: I. The Isotope Effect on Hydrogen Abstraction From Chloroform by the Polystyryl Radical. II. The Transferconstant of Aibn. III. A Scale of Phenyl Affinities.

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I. THE ISOTOPE EFFECT ON HYDROGEN
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POLYSTYRYL RADICAL. II. THE TRANSFER
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I. THE ISOTOPE EFFECT ON HYDROGEN ABSTRACTION FROM
   CHLOROFORM BY THE POLYSTYRYL RADICAL

II. THE TRANSFER CONSTANT OF AIBN

III. A SCALE OF PHENYL AFFINITIES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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Doctor of Philosophy

in

The Department of Chemistry

by

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AIBN  2,2'-Azo-bis-isobutyronitrile
PAT  Phenylazotriphenylmethane
PRT  Primary Radical Termination
R*  Rate of Incorporation of Activity (into Polystyrene or Benzene)
RP  Rate of Polymerization
F  Number-average Degree of Polymerization
S  Solvent
M  Monomer
I  Initiator
A•  Initiator Radical
S•  Solvent Radical
M•  Polymeric Radical, regardless of chain length or mode of initiation (may be AM•)
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ABSTRACT

The dissertation is divided into three main parts.

I. The Isotope Effect on Hydrogen Abstraction from Chloroform by the Polystyryl Radical.

The transfer constants of chloroform-$^3$H and chloroform-$^{14}$C toward the polystyryl radical have been measured by a tracer technique. The values obtained were $6.72 \times 10^{-6}$ and $4.83 \times 10^{-5}$, respectively. This corresponds to a tritium isotope effect of 7.2.

The transfer constants of chloroform and chloroform-$^2$H toward the polystyryl radical have been measured by the classical molecular weight technique. The values obtained were $4.64 \times 10^{-5}$ and $1.10 \times 10^{-5}$, respectively. This corresponds to a deuterium isotope effect of 4.2.

The relationship of the two isotope effects agrees, within experimental error, with that calculated using the Swain equation. The seemingly low isotope effects are rationalized using recent theories of isotope effects.

II. The Transfer Constant of AIBN.

The transfer constant of AIBN toward the polystyryl radical has been measured by a tracer technique. The value obtained was $1.7 \times 10^{-2}$. In an effort to rationalize this high value, a study of model compounds was made. The transfer constants of tetramethylsuccinodinitrile and trimethylacetonitrile toward the polystyryl
radical were determined by the classical molecular weight technique. The values obtained were $3.7 \times 10^{-5}$ and $3.8 \times 10^{-5}$, respectively.

A discussion of the possible reasons for the obtained value of the transfer constant of AIBN is presented. Limits are suggested for the transfer constant of AIBN.

III. A Scale of Phenyl Affinities.

A method has been devised by which the rate of addition of the phenyl radical to olefins is related to the rate of tritium abstraction from heptanethiol-3H. The system allows one to compare the relative affinities of a series of olefins for the phenyl radical.

The relative reactivities obtained show that the polystyryl and methyl radicals are, respectively, 2.37 and 1.73 times more selective than the phenyl radical in additions to olefins. A rationalization for the low selectivity of the phenyl radical is presented.
INTRODUCTION

The dissertation is divided into three parts. Since all three topics are closely related this section provides an introduction for each. The pertinent equations for each topic are derived in the section titled Kinetic Expressions. Each topic may be individually followed through the other sections of the dissertation by reference to the Table of Contents.

It had been the original intent of this study to extend further the existing knowledge of the process termed primary radical termination. The work presented here may best be understood by describing primary radical termination and the experimental procedures designed to study this process.

The normal termination mode in a radical induced polymerization is the combination of two polymeric radicals. In primary radical termination, primary radicals, that is radicals formed by the decomposition of an initiator, enter into termination reactions rather than into initiation reactions.

The four basic reactions involved in a radical induced polymerization may be represented by the following equations:

\[
\begin{align*}
\text{Rate} \\
I & \rightarrow 2A^- & 2k_d[I] \\
A^- + M & \rightarrow M^- & k_i[A^-][M] \\
M^- + M & \rightarrow M & k_p[M^-][M]
\end{align*}
\]
where \( I \) represents the initiator, \( A^\cdot \) the primary radical, \( M \) the monomer, \( M' \) a polymer radical regardless of chain length, and \( P \) a polymer molecule.

If the above reactions are extended to include transfer to a solvent, the following may be added:

\[
\begin{align*}
M^\cdot + SH & \rightarrow P + S^\cdot & k_{tr} [M^\cdot] [SH] \quad (5) \\
S^\cdot + M & \rightarrow M' & k_a [S^\cdot] [M] \quad (6)
\end{align*}
\]

where \( SH \) represents the solvent and \( S^\cdot \) a radical derived by the abstraction of a hydrogen from the solvent by the polymer radical.

In an uninhibited radical polymerization, termination occurs when two radicals meet. In these six reactions there are three different radicals. Reaction 4 depicts the termination reaction, which is the only operative termination under ordinary conditions. However, the termination reactions of interest to this study are those other than Reaction 4.

The termination reaction involving a polymer radical and an initiator radical:

\[
A^\cdot + M^\cdot \rightarrow P \\
\begin{align*}
& \quad k_{ta} [A^\cdot] [M^\cdot] \quad (7)
\end{align*}
\]

is the most probable mode of primary radical termination, as these two radicals are present in relatively high concentrations compared to other possible radicals present. This reaction has been studied rather extensively.
Bamford, Jenkins, and Johnston\(^1\) have studied the 2,2'-azo-bis-isobutyronitrile, AIBN, initiated polymerization of styrene in N,N-dimethylformamide solution. By following the rate of polymerization as a function of initiator and monomer concentrations, they have been able to show deviations from the conventional kinetic scheme. These departures from ideality have been quantitatively accounted for by primary radical termination, that is, Reaction 7.

Manabe, Utsumi, and Okamura\(^2\) have also made a study of Reaction 7. They have studied the bulk polymerization of styrene initiated by AIBN. The molecular weight of the polymer formed was followed as the rate of polymerization was increased. The deviations recorded at high rates of polymerization could be accounted for by Reaction 7, which caused the production of abnormally low molecular weight polymer.

The other termination reactions which are of interest are:

\[
\begin{align*}
A^* + S^* &\rightarrow AS & k_{tas} [A^*][S^*] \quad (8) \\
2A^* &\rightarrow AA & 2k_{t2a} [A^*]^2 \quad (9) \\
S^* + M^* &\rightarrow P & k_{tsm} [S^*][M^*] \quad (10)
\end{align*}
\]

There is little if any knowledge of these reactions in a polymerization system. Of particular interest to this study are Reactions 7, 8, and 9.
Under certain conditions primary radical termination may be made a more favorable process. These conditions have been stated previously by Chapiro. The two main conditions favoring primary radical termination are 1) high radical concentration, and 2) high radical stability, or long radical life. The former is achieved at high initiator concentrations, hence high rates of polymerization. The latter may be achieved in one of three ways. The first method is to use a monomer of low reactivity, which leads to long radical life. The second method is to work at low temperatures, as radicals tend to become more selective at lower temperature, and, therefore, favor termination reactions. Thirdly, one can use dilute monomer solutions, thereby lowering the rate of propagation, Reaction 3, in relation to termination reactions.

A study of Reaction 8, the termination reaction involving solvent and initiator radicals, was attempted first. Chloroform was chosen as a solvent which has a uniquely abstractable hydrogen (see discussion). In one set of experiments, this hydrogen was replaced by tritium and this labelled solvent was used in the AIBN-initiated polymerization of styrene. The rate of incorporation of activity, $R^*$, into the polymer was followed as the rate of polymerization, $R_p$, was increased. In this case, activity was incorporated into the polymer by Reaction 5. A plot of $R^*$ versus $R_p$ yielded a straight line through the whole $R_p$ range studied.
In a second set of experiments, chloroform was labelled with carbon-14 and polymerizations were run as before. Incorporation of activity into the polymer under these conditions is through Reaction 6. Using the R* versus Rplot as above one would expect to obtain a straight line if Reaction 8 does not occur. At high rates of polymerization Reaction 8 may begin to become important and deviation from the straight line would be expected.

As will be seen, the data at high rates of polymerization could not be obtained with high precision. Therefore, the small deviations expected from Reaction 8 could not be detected. However, the isotope effect obtained was of interest. This was checked by the classical molecular weight method. The deuterium and tritium isotope effects agreed, within experimental error, with the prediction from the Swain equation.4

The second attempt to study primary radical termination was concerned with Reaction 7, termination of a polymer radical by an initiator radical, and Reaction 9, the combination of two initiator radicals. Bevington and Lewis5 had postulated that AIBN is not subject to induced decomposition, Reaction 5. Therefore, in the bulk polymerization of styrene initiated by labelled AIBN, the incorporation of activity into the polymer would be by Reaction 2. If primary radical termination is important, Reaction 7 also results in the incorporation of activity. We repeated the experiment of Bevington, but extended the study to higher rates of polymerization2 to look for evidence of Reaction 9.
The results we obtained agree with those of Okamura, but a re-evaluation of Bevington's conclusions became necessary. From the data obtained, it appears that AIBN undergoes considerable induced decomposition. Because of the difficulty encountered in the purification of the polymer, and the resulting lowering of accuracy in the results, a study of model compounds was also made.

From the original attempt to study Reaction 8, it became obvious that not only high rates of polymerization would be required, but a highly reactive solvent would be needed as well. This brought a complication into the original scheme. At high initiator radical concentrations, in the presence of a reactive solvent, abstraction of a hydrogen from the solvent by the initiator radical becomes an important reaction.

\[ A^* + SH \rightarrow AH + S^- \quad k_h \quad [A^*] [SH] \quad (11) \]

This reaction was shown to occur with tritium-labelled heptanethiol as the solvent. At a certain solvent-to-monomer ratio, the initiator radical will partition itself between Reaction 2 and 11. The amount of reaction proceeding by Reaction 11 varies, increasing at higher solvent-to-monomer ratios. We found we were able to utilize this partition between these two reactions to obtain the relative rates of addition of phenyl radicals to a series of polymerizable olefins.

Szwarc and Bink have listed similar data for the relative rates of addition of methyl, ethyl, and propyl radicals to olefins. A comparison of the relative reactivities of these radicals
with the same series of monomers has shown that the phenyl radical shows relatively little selectivity in additions to a series of substituted olefins.
KINETIC EXPRESSIONS

Before discussing the individual projects in detail, it will be convenient to derive all of the equations needed.

**Determination of Transfer Constants**

The mechanism for the radical initiated polymerization of styrene in the presence of a solvent may be summarized as follows:

\[
\begin{align*}
I & \rightarrow 2 A^* & 2k_d [I] \\
A^* + M & \rightarrow M^* & k_i [A^*] [M] \\
M^* + M & \rightarrow M^* & k_p [M^*] [M] \\
2 M^* & \rightarrow P & 2k_t [M^*]^2 \\
M^* + SH & \rightarrow P + S & k_{tr} [M^*] [SH] \\
S^* + M & \rightarrow M^* & k_a [S^*] [M]
\end{align*}
\]

with the same symbolism as used in the introduction. Note that the rate constant for Reaction 1 is written on a per radical basis to conform with conventions in polymerization kinetics. 7

A few simplifying assumptions must be made in order to reduce the kinetic scheme to useful kinetic expressions. It is assumed that all rate constants are independent of chain length. This has
been implied in Reaction 2, so that $AM^* = AM_n^8$. It is also assumed that there is no degradative chain transfer, so that when the solvent radical is formed, Reaction 5, it immediately initiates the growth of a new chain, Reaction 6.

In the determination of a transfer constant, $C = k_{tr}/k_p$, by molecular weight techniques, the termination mechanism must be known. For styrene, much evidence can be cited in support of termination by combination rather than disproportionation. At 25° and 60°, Bevington, Melville, and Taylor\textsuperscript{9,10} have reported that disproportionation is of little significance in the AIBN-initiated polymerization of styrene. Baker and Williams\textsuperscript{11} have shown that the molecular weight distribution in polystyrene produced at 60° conforms almost exactly with that expected from combination as the sole mode of termination. Mayo, Gregg, and Matheson\textsuperscript{12} have also concluded that combination is the main mechanism of termination for the polystyryl radical.

As the amount of polymer produced in a polymerization increases, the amount of transfer to polymer would be expected to increase, leading to chain branching. This complication would cause a lowering of the intrinsic viscosity,\textsuperscript{13,14} which is used for the calculation of molecular weights. For this reason, polymerizations have been run to low conversions.

As the polymerization proceeds, the concentration of reactants is constantly changing. The concentrations ordinarily used are the original concentrations. To increase the accuracy of these results, the concentrations used are calculated to be those when the reaction
is half completed. That is, if the polymerization was carried to 10\% conversion, the concentrations used were those at 5\% conversion.

Useful kinetic expressions have been developed from the kinetic scheme outlined on page 8 and the previously described assumptions.

For radical polymerization processes in which polymer chains are long, most of the monomer is being consumed in the propagation step, Reaction 3. The overall rate of polymerization can be replaced by the rate of propagation.\(^5\)

\[-d [M]/dt = R_p = k_p [M^*] [M]\]  \hspace{1cm} (12)

If one assumes a steady state concentration of radicals, the rate of production of radicals is equal to their rate of destruction:\(^7\)

\[R_i = R_t\]  \hspace{1cm} (13)

so that:

\[ [M^*] = (R_i/2k_t)^{1/2} \]  \hspace{1cm} (14)

The number-average degree of polymerization, \(\bar{P}\), can be defined as the ratio of the number of monomer units to the number of polymer units. In the case in which termination is entirely by combination:\(^15\)

\[\bar{P} = R_p/R_i\]  \hspace{1cm} (15)
and with transfer:

\[ \bar{P} = \frac{R_p}{R_1} + \Sigma \text{ transfer} \]  \hspace{1cm} (16)

Utilizing the steady state approximation, the basic equation for chain transfer to solvent can be derived as: \(^{16}\)

\[ \frac{1}{\bar{P}} = \frac{\delta^2}{[M]^2} R_p + C \frac{[S]}{[M]} \]  \hspace{1cm} (17)

where \( \delta^2 = k_t/k_p^2 \). If \( R_p \) is considered a constant, Equation 17 reduces to the original Mayo equation for transfer to a solvent: \(^{17}\)

\[ \frac{1}{\bar{P}} = \frac{1}{\bar{P}_o} + C \frac{[S]}{[M]} \]  \hspace{1cm} (18)

where \( \frac{1}{\bar{P}_o} \) is the inverse of the degree of polymerization for bulk monomer. Therefore, a plot of the inverse of the number-average degree of polymerization against the solvent-to-monomer ratio yields a straight line with the slope equal to the transfer constant.

The value obtained for \( \frac{1}{\bar{P}} \) comes directly from viscosity measurements. The specific viscosity, \( \eta_{sp} \), was determined at several polymer concentrations according to the relationship:

\[ \eta_{sp} = \frac{t-t_o}{t_o} \]  \hspace{1cm} (19)

where \( t \) is the flow time of the polymer solution through a
viscometer, and $t_o$ is the flow time for pure solvent. The intrinsic viscosity, $[\eta]$, was determined by the method of limiting viscosity. The specific viscosity data as a function of concentration was extrapolated to infinite dilution by means of the Huggins equation:  

$$n_{sp}/C = [\eta] + K [\eta]^2 C$$  \hspace{1cm} (20)

where $C$ is the grams of polymer per 100 ml of solution. This value for $[\eta]$ was used for the determination of $1/\bar{P}$ by equation 21.  

$$1/\bar{P} = 6.2275 \times 10^{-4}/[\eta]^{1.37}$$  \hspace{1cm} (21)

The method for the determination of the transfer constant of a labelled initiator has been previously derived by Bevington and Lewis and is given here in the form derived by Pryor. The transfer step involving an initiator is analogous to that for a solvent (Reactions 5 and 6).

$$M^* + I \longrightarrow \cdot P + I^* \hspace{1cm} k_{tr} [M^*] [I]$$  \hspace{1cm} (22)

$$I^* + M \longrightarrow M^* \hspace{1cm} k_a [I^*] [M]$$  \hspace{1cm} (23)

where $I^*$ is an unspecified radical formed from the attack of the polymer radical on the initiator.
The rate of incorporation of activity, \( R^* = \text{moles of initiator/ l.sec.} \), into the polymer is:

\[
R^* = \frac{1}{2} k_d f \left[ A^* \right] \left[ M \right] + k_{tr} \left[ M^* \right] \left[ I \right]
\]  

(24)

The steady state concentration of primary radicals is:

\[
\left[ A^* \right] = \frac{2 k_d f \left[ I \right]}{k_i \left[ M \right]}  
\]  

(25)

Combining Equations 12, 24, and 25 yields Equation 26.

\[
R^* = k_d f \left[ I \right] + C \frac{\left[ I \right]}{\left[ M \right]} R_p  
\]  

(26)

The labelled initiator concentration, \([I]\), is held constant and \( R_p \) is varied by adding unlabelled initiator. If the rate of incorporation of activity is plotted against the rate of polymerization, the result will be a straight line with an intercept equal to \( k_d f [I] \) and a slope equal to \( C [I] / [M] \).

It should be obvious that using a labelled solvent will modify this equation only to the extent of having a zero intercept, as the only method of incorporation of activity is through the transfer step. The equation for this situation is:

\[
R^* = C \frac{[SH]}{[M]} R_p  
\]  

(27)

The rate of polymerization is calculated by Equation 28.
The rate of incorporation of activity for a labelled initiator is given by:

\[ R^* = \frac{\text{dpm in polymer}}{\text{dpm/mole for initiator}} \times \frac{1}{\text{liter}} \times \frac{1}{\text{sec}} \]  \hspace{1cm} (29a)

while that for a labelled solvent is:

\[ R^* = \frac{\text{dpm in polymer}}{\text{dpm/mole for solvent}} \times \frac{1}{\text{liter}} \times \frac{1}{\text{sec}} \]  \hspace{1cm} (29b)

\[ R_p = \frac{\text{grams of polymer}}{\text{mol. wt. of monomer}} \times \frac{1}{\text{liter}} \times \frac{1}{\text{sec}} \]  \hspace{1cm} (28)

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Determination of Molecular Weights

by Tracer Technique

Since typical polymers consist of many molecular species, molecular weight methods always yield average values. End-group methods of analysis give the number-average molecular weight.

The number-average degree of polymerization, as determined by end-group analysis, is simply the number of moles of monomer in a particular sample divided by the number of moles of initiator incorporated in that polymer sample:

\[ \bar{P} = \frac{\text{moles of monomer used}}{\text{moles of initiator incorporated}} \]  

(30)

assuming termination by combination. The moles of monomer used is calculated as the weight of the polymer sample divided by the molecular weight of the monomer. The moles of initiator incorporated into the polymer is the amount of activity in the polymer divided by the specific activity, dpm/mole, of the initiator. This calculation yields the same result as the equation \( \frac{R_p}{R_i} \) (Equation 15).

This method also gives correct \( \bar{P} \) values when primary radical termination, Reaction 7, becomes operative. A polymer molecule is completed in both Reactions 4 and 7, and by both termination modes a molecule of initiator is incorporated into each polymer molecule.
If the initiator is subject to induced decomposition, and Reactions 22 and 23 incorporate a complete initiator molecule, Equation 30 will still give the correct molecular weight.

It must be noted that the specific activity of the initiator used for these calculations is not the same as that used for the calculation of the transfer constant, Equation 26. The specific activity used here is that for the total initiator present, and not the constant amount of active initiator present in each sample.
Determination of the Relative Rates of Addition of Phenyl Radicals to Polymerizable Olefins

Szwarc and co-workers\textsuperscript{6,22-24} have developed a method for the determination of the relative rates of addition of methyl radicals to various substrates. By decomposing acetyl peroxide in the presence of \textit{iso}-octane and the substrate, A, the formation of methane was compared with that amount formed in pure \textit{iso}-octane.

\begin{align*}
\text{CH}_3^+ + \text{iso-}[C_8H_{18}] & \rightarrow \text{CH}_4 + \text{iso-}[C_8H_{17}] \\
\text{CH}_3^+ + A & \rightarrow \text{CH}_3A^+ 
\end{align*}

By comparison of the amounts of methane formed in each substrate system, the relative "affinity" of the substrate for the methyl radical was determined.

This method, although giving quite good results, has a few inherent problems. Corrections for cage reactions had to be made, i.e., the amount of reaction before the initiator radicals became "free". Also, methane may be formed by methods other than Reaction 31. For many of the substrates used, corrections had to be made for the amount of hydrogen abstraction from the substrate.
itself. Also, when aromatic solvents are used, a second species is present:

![Diagram of a molecule with labels](image)

which may also react with methyl radicals to yield methane.

For the system used in our study, the relative rates of addition of phenyl radicals to various substrates were compared to the abstraction of tritium from tritium-labelled heptanethiol. This removes the complication of benzene being formed by methods other than the phenyl radical reacting with heptanethiol, since any benzene formed by other routes would not be labelled. The amount of reaction with the solvent is monitored by the amount of activity incorporated into the benzene formed.

In this system, phenylazotriphenylmethane, PAT, is decomposed in solutions containing varying ratios of a monomer and tritium-labelled heptanethiol:

\[
\begin{align*}
I & \rightarrow \cdot \phi \\
\cdot \phi + M & \rightarrow \cdot \phi M \\
\cdot \phi + RSH^* & \rightarrow \cdot \phi H^* \\
\cdot \phi + \cdot \phi H & \rightarrow \cdot \phi H
\end{align*}
\]

\[
\begin{align*}
k_{d} [I] & (33) \\
k_{1} [\cdot \phi] [M] & (34) \\
k_{T} [\cdot \phi] [RSH^*] & (35a) \\
k_{H} [\cdot \phi] [RSH] & (35b)
\end{align*}
\]

In this sequance I is PAT, M the monomer, \( \cdot \phi \) a phenyl radical, RSH* labelled heptanethiol and RSH unlabelled heptanethiol.
The rate of formation of benzene is

\[ R_f = d[\cdot H]/dt = k_H[\cdot H][RSH] \]  \hspace{1cm} (36a)

while the rate of formation of labelled benzene is

\[ d[\cdot H^\ast]/dt = k_T[\cdot H][RSH^\ast] = d[\cdot H]/dt \times k_T/k_H \times A_{th} \]  \hspace{1cm} (36b)

in which \( A_{th} = [RSH^\ast]/[RSH] \), which is the specific activity of the thiol. The rate of incorporation of activity into benzene, \( R^\ast \), is now defined by Equation 37.

\[ R^\ast = \frac{\int_0^t d[\cdot H^\ast]/dt}{A_{th}} = R_f k_T/k_H \]  \hspace{1cm} (37)

in which \( \int_0^t d[\cdot H^\ast]/dt \) is the dpm in benzene at time \( t \) in liters/sec.

The steady state approximation in phenyl radicals leads to

\[ R_f = \frac{k_H[RSH] k_{df}[I]}{k_H[RSH] + k_{f}[N]} \]  \hspace{1cm} (38)

which on inversion becomes

\[ \frac{1}{R_f} = \frac{k_{f}[N]}{k_H[RSH] k_{df}[I]} + \frac{1}{k_{df}[I]} \]  \hspace{1cm} (39)

The rate of formation of benzene was determined at different monomer-to-heptanethiol ratios for a series of different fixed concentrations of PAT and reaction times. By plotting the inverse of the rate of formation of benzene versus the monomer-to-heptanethiol ratio, a straight line should be obtained with a slope equal to \( k_{f}/k_H k_{df}[I] \) and an intercept equal to \( 1/k_{df}[I] \). If it is assumed that \( k_{df}[I] \) remains constant from one system to the next, then a comparison
of the slopes for the different monomers will be their relative reactivity towards the phenyl radical.

The assumption that \( k_d f [I] \) remains constant from one system to the next is not completely valid. It is known that related initiators, i.e., \( p \)-nitrophenylazotriphenylmethane and AIBN, decompose at different rates in different substrates.\(^{25,26}\) This is probably the main source of error in this system, as a correct value for \( k_d f \) would be needed for completely accurate results, that is, the initiator was not taken to complete decomposition to avoid changing the monomer and solvent concentrations. Even if a value of \( k_d \) could be determined for each monomer system the determination would probably contain as much error as the assumption that \( k_d \) does not change.

It must also be assumed that the efficiency factor, \( f \), does not change. For the range of PAT concentrations used in this study, the yield of phenyl radicals is quite high.\(^{25,27}\) Therefore, a relatively high change in efficiency will result in only a small change in the overall yield of phenyl radicals. In the presence of reactive species, such as thiols and olefins, PAT would be expected to always give high efficiencies. AIBN, for example, gives nearly constant efficiencies in the presence of thiols.\(^{28}\)

Under the conditions used in this study, the initiator concentration does not remain constant throughout each reaction. The value of \([I]\) can be written:\(^{29}\) 

\[
I = I_o \int_0^t e^{-k_d t} \, dt.
\]
We can then write a new equation in terms of time as the variable.

\[
\frac{1}{R_f} = \frac{k_i[M]}{k_H[RSH]} k_d^f[I] \int_0^t e^{-k_d t} dt + \frac{1}{k_d^f[I] \int_0^t e^{-k_d t} dt}
\]  

(40)

Equation 40 has been checked by comparing the relative reactivities of two different monomers at two different reaction times. The relative reactivities agree quite closely.

The values of the relative affinities displayed by each monomer for the phenyl radical are the slopes obtained from the plot of Equation 40. No attempt has been made to correct for the changing values of the \( k_d^f[I] \) term. (For brevity the value for the initiator concentration at time \( t \) will be simply that described in Equation 39.)

The rate of formation of benzene was calculated by means of Equation 41.

\[
R_f = \frac{k_H}{k_T} R^* 
\]  

(41)

The rate of incorporation of activity into benzene was calculated by means of Equation 42.

\[
R^* = \frac{\text{dpm in benzene}}{\text{dpm/mole for thiol}} \times \frac{1}{\text{liter}} \times \frac{1}{\text{sec}} 
\]  

(42)
EXPERIMENTAL

Preparations and Purifications

Chloroform-³H was prepared by the method of Rodionov and Federova. Trichloroacetic acid (Baker, 30 g, 0.184 mole) and tritiated water (2 ml, 0.111 mole, 42 mc/ml) were added to a flask and the mixture allowed to stir for fifteen minutes. A distillation head was fitted to the flask and freshly distilled dimethylaniline (Merck, 60 g, 0.50 mole) was added. The flask was heated, with stirring, until the chloroform-³H formed had distilled out. The reaction flask was cooled and 4 ml of purified chloroform was added. The flask was again heated and the added chloroform distilled into the same flask. The collected materials were dried over anhydrous sodium sulfate, filtered, and the flask and drying agent washed with three, 3 ml portions of purified chloroform followed by three, 3 ml portions of toluene. The combined fractions were distilled through a 24 cm column packed with Heli-Pak. Prior to use, 6 ml of purified chloroform was added and the mixture distilled through a 20 cm column yielding 23.2 g (0.195 mole) of chloroform-³H, bp 60.9-61.1°, of specific activity 8.465 x 10¹⁰ dpm/mole (11.2% yield on activity).
Chloroform-$^{14}$C (Nuclear Research Chemicals), 1.0 mc (specific activity 1.5 mc/mM) was diluted by vacuum transfer with 12 ml of purified chloroform. Before use, the labelled chloroform was distilled through a 14 cm column packed with Heli-Pak. The yield of Chloroform-$^{14}$C was 16.3 g, bp 61.1-61.8°, of specific activity 5.674 x 10^9 dpm/mole.

Chloroform-$^2$H (Nuclear Magnetic Research Specialties, 99.8% enriched) was distilled, under nitrogen, through a 45 cm Vigreaux column immediately prior to use.

Chloroform was purified as described by Wiberg. Chloroform (Mallinckrodt) was washed with concentrated sulfuric acid, water and saturated sodium bicarbonate solution, followed by drying over anhydrous sodium sulfate. The solution was filtered and the chloroform distilled through a 45 cm Vigreaux column, under nitrogen, immediately prior to use.

Acetone-$^3$H was prepared by preparing a solution of sodium hydroxide (0.2 g) and acetone (Fisher, 8.0 g, 0.136 mole) in tritiated water (30 ml, 1.67 moles, 0.042 mc/ml). This solution was allowed to stir for eight hours, then used as described below.

2,2'-Hydrazo-bis-isobutyronitrile-$^3$H was prepared by the method of Thiele and Heuser. Hydrazine sulfate (10.4 g, 0.08 mole) was mixed in a flask with 60 ml of warm water. To this was added 7.6 g (0.117 mole) of potassium cyanide in 25 ml of water and the solution
allowed to stand for thirty-six hours. The resulting crystals were filtered, washed with distilled water, and dried in a vacuum desiccator.

2,2'-Azo-bis-isobutyronitrile-3H was prepared by the method of Thiele and Heuser.\textsuperscript{32} The hydrazo compound, prepared above, was dissolved in 50 ml of ethanol to which 40 ml of 1:1 hydrochloric acid was then added. The hydrazo compound was oxidized by adding bromine water until a permanent yellow color remained. The product was precipitated, dried and dissolved in ether. The ether solution was washed with concentrated hydrochloric acid, to remove any remaining hydrazo compound, and filtered. The ether layer was dried and the solvent removed. The AIBN was recrystallized twice from absolute ethanol, being careful not to heat the solution above 50°, and dried in a vacuum desiccator. The yield was 3.2 g (28\% from acetone) of 2,2'-azo-bis-isobutyronitrile-3H, mp 104° (lit.\textsuperscript{32} 105°), of specific activity $3.239 \times 10^{9}$ dpm/mole.

Tetramethylsuccinodinitrile was prepared by decomposing AIBN in refluxing toluene for forty-eight hours. The tetramethylsuccinodinitrile was recrystallized twice from absolute ethanol, yielding material with a mp of 168-169° (lit.\textsuperscript{33} 167.0-167.5°).

Trimethylacetonitrile (Eastman Practical Grade) was used without further purification. Analysis by gas chromatography showed it to be more than 99.9\% pure.
**ATBN** (Eastman White Label) was recrystallized twice from absolute ethanol, being careful not to heat the solution above 50°, and dried in a vacuum desiccator.

**Styrene** (Eastman White Label) was allowed to stand over Drierite for twenty-four hours, followed by vacuum distillation. This material was prepolymerized, thermal polymerization under nitrogen to a few percent conversion, and vacuum distilled. The prepolymerization and distillation procedure was repeated immediately prior to use.

**iso-Propylperoxydicarbonate**, IPP, (Lucidol) was dissolved in benzene and dried over anhydrous sodium sulfate. The solution was filtered and frozen. The benzene was removed under vacuum, holding the solution at -10°.

**Heptanethiol-³H**. In a typical preparation, 0.25 ml of tritiated water (42 mc/ml) was mixed with 15 ml heptanethiol (Eastman White Label) and allowed to stir for twenty-four hours. The mixture was then dried over anhydrous sodium sulfate, and the heptanethiol-³H distilled, bp 63° at 15 mm, yielding material of specific activity about 7 x 10¹⁰ dpm/mole. This material was diluted with distilled heptanethiol and redistilled immediately prior to use.

**Phenylazotriphenylmethane** (Eastman White Label), recrystallized by Eastman, was used without further purification. Decomposition of this PAT in pure carbon tetrachloride and subsequent analysis.
by gas chromatography showed the decomposition products to be consistent with previously reported data.²⁵,³⁴

**Allyl acetate** (Eastman White Label) was passed through a column of activated alumina. This material was distilled, immediately prior to use, through a 40 cm Vigreaux column, bp 103.1-103.3°.

**Vinyl acetate** (Eastman Practical Grade) was passed through a column of activated alumina. Immediately prior to use, this material was distilled through a 40 cm Vigreaux column, bp 72.9°.

**Diethyl maleate** (Eastman White Label) was distilled under vacuum before use.

**α-Methylstyrene** (Eastman White Label) was distilled through a 40 cm Vigreaux column, bp 164.3-164.5°.

**2-Vinylpyridine** (Rielly Tar and Chemical Corp.) was vacuum distilled and dried over anhydrous sodium sulfate. After filtration, this material was vacuum distilled from benzoyl peroxide.

**Methacrylonitrile** (Eastman White Label) was dried over anhydrous sodium carbonate. After filtration, this material was distilled through a 40 cm Vigreaux column, bp 88.5-89.5°.

**Methyl acrylate** (Rohm and Haas) was distilled from benzoyl peroxide through a 40 cm Vigreaux column, bp 79.8-80.0°.

**Methyl methacrylate** (Matheson, Coleman, and Bell) was twice distilled from benzoyl Peroxide.
Procedures for Polymerizations

Samples were prepared\textsuperscript{35} by placing the desired amount of reactants in 15 ml glass ampoules. (Drying ampoules sold by Kontes were used). The ampoules were then attached to a vacuum line and the ampoule contents frozen in liquid nitrogen. The ampoules were evacuated to about 0.1 mm, pressured with nitrogen, and the contents melted to de-air. This process was repeated twice. The ampoules were frozen once more and sealed off under vacuum.

Reactions were carried out by immersing the ampoules in a constant temperature bath, $60^\circ \pm 0.01^\circ$, in the dark, for the desired length of time.

Freeze-Drying Procedure

The method used for freeze-drying polymer samples was a modification of the method of Lewis and Mayo.\textsuperscript{36} Polymer samples were transferred from the ampoules, using 20-30 ml of reagent benzene, to tared 125 ml Erlenmeyer flasks. The flask contents were frozen. Freeze-drying was accomplished by attaching the flasks to a vacuum line at about 0.5 mm for sufficient time to remove all volatile portions. The number of freeze-dry cycles, and appropriate times, for each application, will be described in the appropriate discussions below.
Precipitations

Precipitations were carried out in the following fashion. The polymer was dissolved in 20-30 ml of benzene and precipitated by pouring this solution into 250 ml of cold methanol. Methanol temperatures will be described in appropriate sections. This solution was filtered using Whatman No. 2 filter paper.

Extractions

Because the precipitation procedure, above, gives rise to the loss of polymer, an extraction procedure for polymer purification was developed. The polymer was first dissolved in about 75 ml of benzene, then freeze-dried to constant weight (about 36 hours). A measured amount of polymer was then transferred to a Soxhlet-like thimble prepared from Whatman No. 1 filter paper.

When extracting with pentane, the thimble was placed in a Soxhlet extractor. Pentane was then refluxed through the apparatus for eight hours. The thimble was removed and the remaining pentane allowed to evaporate. The thimble was then placed in an ordinary funnel which had been fitted with a stopcock and allowed to soak in benzene until the polymer dissolved. The solution was drained into an Erlenmeyer flask and the funnel thoroughly rinsed with benzene.
When extracting with methanol, the polymer was placed in the thimble as before. The thimble was placed in the filter funnel, described above, and $0^\circ$ methanol was added. The polymer was allowed to soak for one hour. The methanol was drained off and more added. This process was repeated for a total of eight one-hour periods. The polymer was then recovered as described for pentane extractions.

It was evident that these extraction procedures also gave rise to loss of polymer. Of the two procedures, the methanol method gave better polymer retention by about 40%. For extractions involving about 0.75 g of polymer, the average loss of polymer was 24 mg for pentane extractions, and 16 mg for methanol extractions.

**Procedures for Viscosities**

Specific viscosities were determined in the following fashion. A measured amount (50-70 mg) of polymer was placed in a 25 ml volumetric flask. Filtered benzene was added and the polymer allowed to dissolve. The flask was placed in a constant temperature bath, $30^\circ \pm 0.03^\circ$, and the flask filled with filtered benzene. The polymer solution was then filtered. The viscosity was then determined, at $30^\circ$, in a Ubbelohde-type viscometer, Cannon No. 75/115. The solution, in the viscometer, was then diluted with filtered benzene and the viscosity determined again. The dilution and viscosity determination process was repeated to give a total of four specific
viscosities at four concentrations. Polymer solutions were used such that flow times were long enough to be able to ignore kinetic energy considerations.  

Counting Radioactive Polymer

To the polymer in the Erlenmeyer flask was added 8 ml of liquid scintillation solution, made by diluting Packard Concentrated Liquid Scintillator, No. 6003004. The polymer was allowed to dissolve. This solution was then transferred to a liquid scintillation counting vial, by Packard. The Erlenmeyer flask was rinsed with two 5-ml portions of liquid scintillation solution, adding these portions to the same counting vial. The amount of activity was determined in a Packard Liquid Scintillation Spectrometer, No. 3365, with automatic external standardization. All activities are reported as disintegrations per minute, dpm.
Polymer Purification Procedures for the Isotope Effect on the Transfer Constant of Chloroform

Chloroform-^3H_ polymer samples were purified by the following procedure. After polymerization, the ampoule contents were transferred to a tared Erlenmeyer flask, using about 20-30 ml of reagent benzene. To this was added 1 ml of inactive chloroform. This mixture was freeze-dried for twelve hours. The polymer was then precipitated three times from -30° methanol. The polymer was then freeze-dried for five four-hour periods, with about 0.5 ml of inactive chloroform being added to the polymer solution each time. The polymer was then extracted three times with methanol. The obtained polymer was then freeze-dried for twenty-four hours. The polymer weight was recorded and the amount of activity in the polymer determined.

Controls were run using this same procedure, with the exception that toluene was used in place of labelled chloroform in the preparation of unlabelled polymer. After opening the ampoule, the same amount of labelled chloroform, as used in the kinetic runs, was added to the ampoule and the purification procedure, described above, was followed. The amount of activity present, above background, is shown in Table 1. Since the amount of activity present

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in the controls was very low, no correction for the activity in the kinetic runs was made.

The percent recovery of polymer during the precipitation and extraction procedures is quite high, usually greater than 98%. The only large loss of polymer is due to transfer of the polymer to the Soxhlet thimble. This amount has been determined and the corresponding polymer weights were corrected by this amount. The activity incorporated into the polymer was assumed to be low by the same percentage as the polymer weights. The activity was, therefore, corrected by this same percentage.

Chloroform-C-14 polymer samples were purified by the following procedure. The ampoule contents were transferred, using 20-30 ml of reagent benzene, to a tared Erlenmeyer flask. The samples were freeze-dried for five twelve-hour periods, adding 1 ml of inactive chloroform to the solution before each of these processes. The polymer was then extracted three times with pentane followed by three methanol extractions. The polymer was then precipitated twice from -30° methanol followed by freeze-drying for twenty-four hours. The polymer weight was recorded and the amount of activity incorporated into the polymer determined.

Controls were run using this same procedure. Preparation of unlabelled polymer was done in the fashion described for chloroform-3H. The residual activity for each sample is shown in Table 1. Because the amount of activity remaining is fairly high in relation to the
400–500 dpm present in kinetic runs, 24 dpm was subtracted from the amount of activity in each of the samples used for the determination of the rate of incorporation of activity. This correction could account for a ±5% inaccuracy in the results. The polymer weights and activities were corrected in the same fashion as described for chloroform-$^3$H samples.

Chloroform and chloroform-$^2$H polymer samples were purified in the following fashion. The ampoule contents were transferred to an Erlenmeyer flask and freeze-dried until all volatile portions had been removed. The polymer was then freeze-dried for two twenty-four hour periods. Viscosities were then determined as previously described.

Table 1
Residual Activity in Controls for the Purification of Labelled Chloroform Polymer Samples

<table>
<thead>
<tr>
<th>Run</th>
<th>R$_P$ x10$^4$ at which polymer was formed</th>
<th>Residual activity, dpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H-1</td>
<td>0.42</td>
<td>1</td>
</tr>
<tr>
<td>$^3$H-2</td>
<td>2.02</td>
<td>4</td>
</tr>
<tr>
<td>$^3$H-3</td>
<td>3.30</td>
<td>4</td>
</tr>
<tr>
<td>$^3$H-4</td>
<td>4.58</td>
<td>6</td>
</tr>
<tr>
<td>$^{14}$C-1</td>
<td>0.50</td>
<td>15</td>
</tr>
<tr>
<td>$^{14}$C-2</td>
<td>1.85</td>
<td>34</td>
</tr>
</tbody>
</table>

Average 24
Polymer Purification Procedures for AIBN

and Related Transfer Constants

For the determination of the transfer constant of AIBN, samples were prepared in the following fashion. The desired amount of labelled AIBN was added to a volumetric flask and the flask filled with styrene. To insure reproducibility of this process, each time solutions were prepared, the same volumetric flask was used, and the temperature of the flask, and the styrene, was kept constant at 20°. The desired amount of unlabelled AIBN was then placed in ampoules. The styrene-labelled-AIBN solution was then transferred, by volumetric pipet, into each ampoule at 20° using the same pipet each time. The ampoules were de-aired, sealed and placed in a 60°, ± 0.01°, bath for the desired length of time. Upon removal from the bath, the ampoules were cooled in a Dry-Ice-acetone bath. The ampoule contents were transferred to a tared Erlenmeyer flask and freeze-dried to remove the volatile portions. The polymer was then precipitated four times from -10° methanol, followed by freeze-drying for twenty-four hours. About 200 mg of unlabelled AIBN was added after the first and second precipitations to help in the removal of labelled AIBN. The polymer weight was recorded and the activity incorporated into the polymer determined. Loss of polymer could be minimized by using colder methanol in the precipitation.
procedure, however, AIBN is insoluble in cold alcohol and the re-
moval of activity was not sufficient when using methanol at lower 
temperatures.

Controls were run to calculate the amount of residual activity 
in the polymer from incomplete removal of AIBN. These data are 
presented in Table 2. An average of 28 dpm was subtracted from 
the amount of activity determined to be in each sample used in the 
determination of the transfer constant.

Polymer recovery was about 95% from the four precipitations. 
However, this amount was not corrected in the final results. Cor-
rection for lost polymer would be difficult as most samples contain 
a significant amount of AIBN, and AIBN is added during the precipitation 
procedures.

Tetramethylsuccinodinitrile polymer samples were purified by 
the following procedure. The ampoule contents were transferred 
to a tared Erlenmeyer flask. The samples were then precipitated 
twice from -10° methanol, followed by freeze-drying for twenty-four 
hours. Viscosities were then determined as previously described.

Trimethylacetonitrile polymer samples were purified in the 
following fashion. The ampoule contents were transferred to a 
tared Erlenmeyer flask, and freeze-dried to remove the volatile 
portions. The polymer was then freeze-dried for two twenty-four 
hour periods. Viscosities were determined as previously described.
Because the precipitation procedure for purification of polystyrene gives rise to loss of polymer and the data for the transfer constant at 60° lacked high precision, the determination of the transfer constant at 30° was attempted. A solution of IPP in acetone was prepared. The desired quantities of this solution were transferred into ampoules. The acetone was removed, under vacuum, while holding the ampoule at -10°. A solution of labelled AIBN in styrene was then added to the ampoules. The ampoules were then de-aired and sealed as previously described. The ampoules were then placed in a 30°, ± 0.03°, bath for the desired length of time. Upon removal of the ampoules from the bath, the polymer was immediately precipitated from 0° methanol. The polymer was then extracted three times with methanol. The weight was recorded and amount of activity incorporated into the polymer was determined.

A control was prepared to determine the amount of activity remaining after purification of the polymer. The amount of activity in this control was 2,075 dpm. This amount was subtracted from the amount of activity determined to be present in each of the kinetic runs.

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual Activity in Controls for the Purification of Labelled AIBN Polymer Samples Run at 60°</td>
</tr>
<tr>
<td>Run</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Procedures for the Determination of Phenyl Affinities

Samples were prepared, placed in ampoules, de-aired, and reactions carried out as described in the procedures for polymerizations. The ampoules were wrapped in aluminum foil during preparation and reaction periods to insure no photolytic decomposition of the initiator. When the ampoule had been in the constant temperature bath, 60° ± 0.01°, for the desired length of time, the ampoule was removed and cooled in liquid nitrogen. The ampoule was opened and a measured amount of benzene was added. This was allowed to equilibrate with the reaction mixture. This solution was then transferred to a 50 ml flask wrapped in aluminum foil. The volatile portions were transferred under vacuum, <0.01 mm, to a second flask. This material was then treated as described in Table 3, to obtain purified benzene. A measured amount, about 2 ml, of the purified benzene was added to 16 ml of liquid scintillation solution and the amount of activity present was determined as previously described.

Controls were run for each monomer system. These were prepared as in the case of actual rate-determination samples, with the exception that the controls were not placed in the 60° bath. These controls were then taken through the same purification procedure.
as described for each monomer. The amount of activity present in the purified benzene was plotted against the heptanethiol concentration. These data gave a reasonably straight line (see, for example, Table 4 and Figure 1). The amount of activity determined to be in each rate sample was corrected for the amount of activity present, or calculated to be present, for a control having the same heptanethiol concentration.

To insure that no activity is removed from the labelled benzene, a control was run in the following fashion. A synthetic mixture was prepared using labelled benzene and styrene. This was taken through the purification procedure described for styrene samples, Table 3. The specific activity of the benzene was determined before and after the purification. The specific activity was lower, after purification, by 0.08%. This amount is probably due to experimental error.

To determine the tritium isotope effect, $k_H/k_T$, for the abstraction of hydrogen from heptanethiol by the phenyl radical, samples were prepared, with varying amounts of PAT, in both heptanethiol and heptanethiol-$^3$H. These samples were placed in the 60° bath for six hours, sufficient time to essentially destroy the initiator. The heptanethiol samples were then analyzed by gas chromatography, see Table 3 for conditions, for amount of benzene formed. The heptanethiol-$^3$H samples were treated as
described for styrene samples in Table 3, except that the wash with bromine water was omitted, and the amount of activity in the benzene was determined.
Table 3

Methods of Purification of Benzene for the Determination of
Relative Reactivities of Olefins Towards the Phenyl Radical

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Purification Method</th>
<th>Impurities b</th>
<th>Column and Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>A</td>
<td>None detectable</td>
<td>SE-30; 50°</td>
</tr>
<tr>
<td>α-Methylstyrene</td>
<td>A</td>
<td>None detectable</td>
<td>SE-30; 50°</td>
</tr>
<tr>
<td>Vinyl Acetate</td>
<td>B</td>
<td>None detectable</td>
<td>BDIP; 53°</td>
</tr>
<tr>
<td>Allyl Acetate</td>
<td>B</td>
<td>None detectable</td>
<td>BDIP; 53°</td>
</tr>
<tr>
<td>Methyl Acrylate</td>
<td>B</td>
<td>0.1%</td>
<td>QF-1; 43°</td>
</tr>
<tr>
<td>Methyl Methacrylate</td>
<td>C</td>
<td>0.1%</td>
<td>QF-1; 43°</td>
</tr>
<tr>
<td>Methacrylonitrile</td>
<td>D</td>
<td>0.1%</td>
<td>QF-1; 43°</td>
</tr>
<tr>
<td>Diethyl Maleate</td>
<td>A*</td>
<td>None detectable</td>
<td>SE-30; 50°</td>
</tr>
<tr>
<td>2-Vinyl Pyridine</td>
<td>A</td>
<td>None detectable</td>
<td>SE-30; 50°</td>
</tr>
</tbody>
</table>

a) All purification procedures are preceded by a vacuum transfer of the more volatile portions to a separate flask.

b) Impurities, initial monomer and heptanethiol, were not detected in most cases. The only places where impurities were detected were in instances where the monomer was separated from the benzene by repeated washings. These washings were continued until the monomer was present to no more than the stated amount.

c) The gas chromatograph used was a Microtek 2000R.
Purification Methods.

A. The mixture was distilled through a 10 cm. glass-bead packed column collecting the material with a bp to 81°. This fraction was then stirred for one hour with an equal volume of bromine water. The mixture was then washed with 200 ml of 10% sodium hydroxide solution followed by washing with two 200-ml portions of 5% sodium chloride solution. The organic layer was dried over anhydrous sodium sulfate and distilled through a 10 cm column. (* Diethyl maleate was washed twice with base solution).

B. The solution was distilled through a 10 cm column, collecting all material with a bp up to 81°. This material was washed with two 200-ml portions of 10% sodium hydroxide solution and two 200-ml portions of 5% sodium chloride solution. After drying over anhydrous sodium sulfate, the benzene was distilled through a 10 cm column.

C. Same as B except solution washed four times with base.

D. Same as B except solution washed five times with sodium chloride solution.
<table>
<thead>
<tr>
<th>Run</th>
<th>[RSH]</th>
<th>dpm, Residual Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.067</td>
<td>498</td>
</tr>
<tr>
<td>2</td>
<td>0.138</td>
<td>943</td>
</tr>
<tr>
<td>3</td>
<td>0.245</td>
<td>1,761</td>
</tr>
</tbody>
</table>
Figure 1. Residual Activity in Benzene for Controls Using Methacrylonitrile

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RESULTS AND DISCUSSION

The Kinetic Isotope Effect for the Abstraction of Hydrogen from Chloroform by the Polystyryl Radical

The chain transfer step in a radical-initiated polymerization is depicted by Reactions 5 and 6.

\[ M^- + \text{SH} \rightarrow P + S^- \quad k_{\text{tr}}[M^-][\text{SH}] \quad (5) \]

\[ S^- + M \rightarrow M^- \quad k_a[S^-][M] \quad (6) \]

If the abstracted solvent hydrogen is labelled with tritium, SH*, activity is incorporated into the polymer by Reaction 5. The rate constant, \( k_{\text{tr}} \), for this reaction is the rate of abstraction of tritium. If the solvent is labelled with carbon-14, SH*, activity is incorporated into the polymer through Reaction 6. The rate constant, \( k_a \), for this process is not measured. However, if one assumes the steady state approximation the rates of reactions 5 and 6 are equal. The actually measured rate constant is for hydrogen abstraction, \( k_{\text{tr}} \), in Reaction 5, assuming no degradative transfer.

The ratio of the results obtained for the transfer constant of a solvent labelled in these two ways will give the tritium isotope effect, \( k_{\text{H}}/k_{\text{T}} \), for Reaction 5.

Chloroform was the solvent chosen to be used in this experiment. It must be demonstrated that the attack of the polystyryl radical on chloroform results in the abstraction
of hydrogen. If a significant amount of chlorine abstraction took place, then the comparison of the results would not lead to the correct value of the tritium isotope effect.

From a study of the literature on radical reactions involving chloroform, the following conclusions can be made. If the attacking species is a non-carbon radical, chlorine abstraction is usually the favored process. For instance, in the photolysis of pentaphenylphosphorane, the products consist of 65% benzene and a quantitative yield of tetraphenylphosphonium chloride.\(^{38}\) Also, in the thermolysis of dicyclopentadienyl(dimethyl)titanium in chloroform, the only product isolated, resulting from attack by titanium, was dichlorodicyclopentadienyltitanium.\(^{39}\)

If the attacking species is a radical on carbon, the favored process is hydrogen abstraction. In the radical addition of chloroform to norbornene\(^{40}\) and norbornadiene,\(^{41}\) the only products isolated resulted from hydrogen abstraction. In the radical telomerization of ethylene, with chloroform as the transfer agent, the only low molecular weight species isolated and characterized resulted from abstraction of hydrogen.\(^{42}\) Cadogan, Hey, and Hibbert\(^{43}\) have studied the reactions of phenyl, \(p\)-nitrophenyl, \(p\)-chlorophenyl, \(p\)-methylphenyl and hexyl radicals with chloroform. In the case of phenyl and substituted phenyl radicals, chlorine abstraction amounts to about 0.5% of the reaction. In the case of the hexyl radical, there is 1.0% chlorine abstraction.
From the above presented evidence the conclusion may be drawn that the attack on chloroform by the polystyryl radical should lead to only an insignificant amount of chlorine abstraction.

The results for the AIBN-initiated polymerization of styrene in the presence of chloroform-\(^{3}\text{H}\) are presented in Tables 6 and 7, and in Figure 2. The transfer constant obtained for the abstraction of tritium from chloroform-\(^{3}\text{H}\) by the polystyryl radical was \(6.7 \times 10^{-6}\).

The results for the AIBN-initiated polymerization of styrene in the presence of chloroform-\(^{14}\text{C}\) are presented in Tables 8 and 9, and Figure 3. The transfer constant obtained for the abstraction of hydrogen from chloroform-\(^{14}\text{C}\) by the polystyryl radical was \(4.8 \times 10^{-5}\).

The comparison of these results gives a tritium isotope effect, \(k_\text{H}/k_\text{T}\), of 7.2. Because of the possibility of fractionation of molecular weight species during the precipitation and extraction processes 44,45 these results were checked by the classical molecular weight technique.

The results for the thermal polymerization of styrene in the presence of chloroform are presented in Table 10 and Figure 4. The transfer constant obtained for the abstraction of hydrogen from chloroform by the polystyryl radical was \(4.6 \times 10^{-5}\).

The results for the thermal polymerization of styrene in the presence of chloroform-\(^{2}\text{H}\) are presented in Table 11 and Figure 5.
The transfer constant obtained for the abstraction of deuterium from chloroform-$^2$H by the polystyryl radical was $1.1 \times 10^{-5}$.

Comparison of these results yields a deuterium isotope effect, $k_H/k_D$, of 4.2. The difference between the deuterium and tritium isotope effects for a normal primary isotope effect is given by the Swain equation:  

$$k_H/k_T = (k_H/k_D)^{1.442}$$

The range of $k_H/k_T$ and $k_H/k_D$ values, calculated from the most probable errors, are tabulated in Table 5. By use of the Swain equation, the values of $k_H/k_D$ were calculated at the limits of $k_H/k_T$ determined from the most probable error. This range overlaps the $k_H/k_D$ range of error. The center value of this overlapping region was calculated to be a $k_H/k_D$ value of 4.13. This should be the best value from the two sets of data. The corresponding value of $k_H/k_T$ is 7.69.

The only other data for the isotope effect on hydrogen abstraction by the polystyryl radical are for n-butanethiol. The value obtained for $k_H/k_D$, at 60°, was 4.0. This is quite close to the value obtained here for chloroform and seems to be somewhat unusual as the value for the two transfer constants varies by $4 \times 10^5$, the value for n-butanethiol is 21.

To explain the similarity of the two isotope effects requires a discussion of isotope effect theory. The first, or basic, theory
of isotope effects was put forth by Eyring. Eyring's theory assumes that the reactants are in equilibrium with an activated complex, or transition state, which subsequently decomposes, in the rate determining step to the products. This activated complex is distinguished from ordinary molecules in that one of its vibrations has been replaced by an internal translation, which is usually considered to be the vibrational frequency corresponding to the reaction coordinate. For example, in the abstraction of hydrogen from A-H by the species B⁻, the lost vibrational frequency is that of A-H, which becomes

\[ \text{A} \rightarrow \text{H} \rightarrow \text{B} \]

at the transition state.

According to Eyring, the largest portion of the kinetic isotope effect originates with changes in zero-point energy which arise when the reactants are converted to the transition state. The stretching vibration of A-H is associated with a frequency \( \nu_H \) and has a zero-point energy of \( \frac{1}{2} \hbar \nu_H \). Similarly, the stretching frequency for A-D has a frequency \( \nu_D \) and a zero-point energy of \( \frac{1}{2} \hbar \nu_D \). An ordinary C-H bond has a stretching frequency of about 2,900 cm\(^{-1}\) and that for C-D is about 2,100 cm\(^{-1}\). The zero-point energies associated with these two frequencies are 4.15 and 3.00 kcal/mole respectively. If in the transition state this stretching frequency becomes a degree of translational freedom, the
vibration is lost, and \( v^*_H \) and \( v^*_D \), the corresponding stretching frequencies for the transition state, become zero. The difference between the abstraction of hydrogen and deuterium, from A-H or A-D, is then the difference between the zero-point energies for A-H and A-D, or 1.15 kcal/mole, as in the case of the ordinary C-H bond. This corresponds, at 25°, to a rate difference of seven. This theory cannot easily explain smaller ratios of \( k_H/k_D \), as obtained here for chloroform and by Wall for \( n \)-butanethiol.

A more recent treatment of the kinetic isotope effect is present by Bell. If the transition state is regarded as a linear, tri-atomic species, its normal modes of vibration can be represented:

Unsymmetrical Stretch

\[
\begin{align*}
+ & \quad + \\
A & \quad \quad \quad \quad H \quad \quad \quad \quad B \quad (\text{imaginary frequency } v_3, \text{reaction coordinate})
\end{align*}
\]

Symmetrical Stretch

\[
\begin{align*}
+ & \quad ? \\
A & \quad \quad \quad \quad H \quad \quad \quad \quad B \quad (v_1, \text{motion of } H \text{ indeterminate})
\end{align*}
\]

Bending

\[
\begin{align*}
+ & \quad + \\
A & \quad \quad \quad \quad H \quad \quad \quad \quad B \quad (v_2, \text{doubly degenerate})
\end{align*}
\]

The first attempts to explain low isotope effects, such as obtained here, supposed that at the transition state, some of the bond character of A-H was retained, so that some of the original zero-point energy was still present. This, as pointed out by
Westheimer, is equivalent to saying that there is a real value for $v_3$. This is inconsistent with transition state theory, which says that the transition state must have one normal mode corresponding to a maximum in the energy surface, the path over which the atom is transferred, and hence lacking a real vibration. Westheimer further points out that when the force constants for A--H and H--B are unequal, the symmetrical stretching frequency, $v_1$, will involve considerable motion of the atom and will, therefore, be a source of mass-dependent, zero-point energy. This view has been generally adopted and from this comes the prediction that in a series of similar reactions, $k_H/k_D$ will have a maximum value when the transition state is symmetrical. A symmetrical transition state is considered to be one in which the force constants between the end atoms and the atom being transferred are balanced so that the atom being transferred is not involved in the symmetrical stretching vibration, $v_1$.

If one considers the data obtained here for chloroform, and by Wall for n-butanethiol in the light of the preceding discussion, the similarity of the results may be rationalized in the following manner. The ordinary stretching frequency for a C-H bond is in the neighborhood of 2,800-2,900 cm$^{-1}$. If the stretching frequency, for the C-H bond being formed when the polystyryl radical abstracts a hydrogen, is considered to have an ordinary frequency, and the
C-H bond being broken in the abstraction process has an ordinary frequency, a large isotope effect would be expected.

The stretching frequency of the S-H bond for \( \text{\textit{n}} \)-butanethiol\(^{52} \) is 2,590 cm\(^{-1} \). This alone would predict from Eyring's theory that the kinetic isotope effect would be smaller than the maximum value of seven due to the smaller amount of zero-point energy. From, the more advanced theory described by Bell, the difference between the stretching frequency of the bond being formed, 2,800-2,900 cm\(^{-1} \), and the bond being broken, 2,590 cm\(^{-1} \), would also account for the low isotope effect due to an unsymmetrical transition state.

The stretching frequency for the C-H bond of chloroform\(^{53} \) is 3,021 cm\(^{-1} \). This would also lead to an unsymmetrical transition state.

From the preceding discussion, it can be seen that an unsymmetrical transition state predicts a mass-dependent, zero-point energy in the transition state, as the hydrogen atom will have considerable motion in the symmetrical stretching frequency \( \nu_1 \). Therefore, both isotope effects should be lower than the maximum value, as is observed.

It would be of interest to further extend the number of isotope effects for hydrogen abstraction by the polystyryl radical to include compounds, whose stretching frequencies for the broken C-H bond more closely approximate an ordinary C-H stretching frequency.
The values for $C_s$ in the first and third columns of Table 5 are the rates of abstraction of hydrogen depicted by Reaction 5. These two values agree quite well even though they were determined by two completely different methods. The value of $C_s$, about $5 \times 10^{-5}$, is in close agreement with previously reported values of the transfer constant of chloroform. ($5.0 \times 10^{-5}$, Ref. 99; $5.7 \times 10^{-5}$, Ref. 100).

Table 5. Summary of Kinetic Isotope Effect on the Abstraction of Hydrogen from Chloroform by the Polystyryl Radical

<table>
<thead>
<tr>
<th>Method</th>
<th>$^{14}C$</th>
<th>$^{3}H$</th>
<th>$H$</th>
<th>$^{2}H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_s$</td>
<td>$4.83 \times 10^{-5}$</td>
<td>$6.72 \times 10^{-6}$</td>
<td>$4.64 \times 10^{-5}$</td>
<td>$1.10 \times 10^{-5}$</td>
</tr>
<tr>
<td>Most Probable</td>
<td>±$0.25 \times 10^{-5}$</td>
<td>±$0.15 \times 10^{-6}$</td>
<td>±$0.07 \times 10^{-5}$</td>
<td>±$0.10 \times 10^{-5}$</td>
</tr>
<tr>
<td>Error</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isotope Effect</td>
<td>$k_H/k_T = 6.67-7.73$</td>
<td></td>
<td>$k_H/k_D = 4.12-4.33$</td>
<td></td>
</tr>
<tr>
<td>Best Value of</td>
<td>$k_H/k_T = 7.69$</td>
<td></td>
<td>$k_H/k_D = 4.13$</td>
<td></td>
</tr>
<tr>
<td>Isotope Effect(^a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Calculated by method described on p. 47.
Table 6. Corrected Molarities for the AIBN-Initiated Polymerization of Styrene at 60° in the Presence of Chloroform-$^3$H\textsuperscript{a}

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Volume, ml</th>
<th>[M]\textsuperscript{b}</th>
<th>[SH]</th>
<th>[I]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.289</td>
<td>6.928</td>
<td>1.513</td>
<td>6.44x10\textsuperscript{-3}</td>
</tr>
<tr>
<td>2</td>
<td>8.310</td>
<td>6.912</td>
<td>1.509</td>
<td>2.72x10\textsuperscript{-2}</td>
</tr>
<tr>
<td>3</td>
<td>8.342</td>
<td>6.887</td>
<td>1.504</td>
<td>5.98x10\textsuperscript{-2}</td>
</tr>
<tr>
<td>4</td>
<td>8.382</td>
<td>6.854</td>
<td>1.496</td>
<td>1.02x10\textsuperscript{-1}</td>
</tr>
<tr>
<td>5</td>
<td>8.441</td>
<td>6.808</td>
<td>1.486</td>
<td>1.62x10\textsuperscript{-1}</td>
</tr>
<tr>
<td>6</td>
<td>8.599</td>
<td>6.682</td>
<td>1.457</td>
<td>3.23x10\textsuperscript{-1}</td>
</tr>
<tr>
<td>7</td>
<td>8.691</td>
<td>6.609</td>
<td>1.441</td>
<td>4.17x10\textsuperscript{-1}</td>
</tr>
<tr>
<td>8</td>
<td>8.808</td>
<td>6.516</td>
<td>1.420</td>
<td>5.37x10\textsuperscript{-1}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Volumes and molarities have been calculated at half reaction.

\textsuperscript{b} [M]/[S] = 4.58.
Table 7. The AIBN-Initiated Polymerization of Styrene at 60° in the Presence of Chloroform-3H

<table>
<thead>
<tr>
<th>Run</th>
<th>Sec x 10^-3</th>
<th>Grams Polymer</th>
<th>R_p x 10^4</th>
<th>dpm in Polymer</th>
<th>R* x 10^10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.62</td>
<td>0.7960</td>
<td>0.47</td>
<td>869</td>
<td>0.64</td>
</tr>
<tr>
<td>2</td>
<td>8.70</td>
<td>0.7228</td>
<td>0.96</td>
<td>770</td>
<td>1.27</td>
</tr>
<tr>
<td>3</td>
<td>6.12</td>
<td>0.7550</td>
<td>1.42</td>
<td>886</td>
<td>2.07</td>
</tr>
<tr>
<td>4</td>
<td>4.62</td>
<td>0.7420</td>
<td>1.84</td>
<td>895</td>
<td>2.75</td>
</tr>
<tr>
<td>5</td>
<td>3.60</td>
<td>0.7310</td>
<td>2.31</td>
<td>853</td>
<td>3.34</td>
</tr>
<tr>
<td>6</td>
<td>2.64</td>
<td>0.7565</td>
<td>3.20</td>
<td>840</td>
<td>4.41</td>
</tr>
<tr>
<td>7</td>
<td>2.22</td>
<td>0.7233</td>
<td>3.60</td>
<td>863</td>
<td>5.32</td>
</tr>
<tr>
<td>8</td>
<td>1.92</td>
<td>0.7079</td>
<td>4.03</td>
<td>829</td>
<td>5.84</td>
</tr>
</tbody>
</table>

a) Calculated before purification of polymer.

b) This is the total calculated dpm. This number has been calculated as the actual dpm counted times the actually produced grams of polymer over the grams of polymer counted after polymer purification.

c) The specific activity of the chloroform-3H is 8.401 x 10^10 dpm/mole.

d) A least square treatment of a plot of Equation 27 for this data yields R* = 1.46 x 10^-6 R_p - 0.05 x 10^-10. The transfer constant for chloroform-3H is then 6.7 x 10^-6.

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Figure 2. Graph of $R^*$ vs. $R_p$ for the AIBN Initiated Polymerization of Styrene at 60° in the Presence of Chloroform-$^3$H

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Table 8. Corrected Molarities for the AIBN-Initiated Polymerization of Styrene at 60° in the Presence of Chloroform-$^{14}$Ca

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Volume, ml</th>
<th>[M]$^b$</th>
<th>[SH]</th>
<th>[I]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.289</td>
<td>6.928</td>
<td>1.513</td>
<td>6.53x10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>8.309</td>
<td>6.912</td>
<td>1.509</td>
<td>2.67x10^{-2}</td>
</tr>
<tr>
<td>3</td>
<td>8.342</td>
<td>6.887</td>
<td>1.504</td>
<td>5.98x10^{-2}</td>
</tr>
<tr>
<td>4</td>
<td>8.386</td>
<td>6.851</td>
<td>1.496</td>
<td>1.05x10^{-1}</td>
</tr>
<tr>
<td>5</td>
<td>8.445</td>
<td>6.804</td>
<td>1.485</td>
<td>1.66x10^{-1}</td>
</tr>
<tr>
<td>6</td>
<td>8.516</td>
<td>6.749</td>
<td>1.472</td>
<td>2.38x10^{-1}</td>
</tr>
</tbody>
</table>

a) Volumes and molarities have been calculated at half reaction.

b) $[M]/[SH] = 4.58$. 

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Table 9. The AIBN-Initiated Polymerization of Styrene at 60° in the Presence of Chloroform-\(^{14}\)C

<table>
<thead>
<tr>
<th>Run</th>
<th>Sec(\times10^{-3})</th>
<th>Grams Polymer(^a)</th>
<th>(R\times10^4)</th>
<th>dpm in Polymer(^b,c)</th>
<th>(R^a\times10^9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.62</td>
<td>0.7960</td>
<td>0.47</td>
<td>418</td>
<td>0.45</td>
</tr>
<tr>
<td>2</td>
<td>9.18</td>
<td>0.7546</td>
<td>0.95</td>
<td>408</td>
<td>0.94</td>
</tr>
<tr>
<td>3</td>
<td>6.12</td>
<td>0.7550</td>
<td>1.42</td>
<td>506</td>
<td>1.75</td>
</tr>
<tr>
<td>4</td>
<td>4.62</td>
<td>0.7542</td>
<td>1.87</td>
<td>458</td>
<td>2.08</td>
</tr>
<tr>
<td>5</td>
<td>3.60</td>
<td>0.7409</td>
<td>2.34</td>
<td>404</td>
<td>2.34</td>
</tr>
<tr>
<td>6</td>
<td>3.00</td>
<td>0.7396</td>
<td>2.78</td>
<td>428</td>
<td>2.95</td>
</tr>
</tbody>
</table>

a) Calculated before purification of polymer.

b) This is the total calculated dpm. This number has been calculated as the actual dpm counted times the actually produced grams of polymer over the grams of polymer counted after polymer purification. (Corrected for background, p. 32).

c) The specific activity of the chloroform-\(^{14}\)C is 5.674\(\times10^9\) dpm/mole.

d) A least square treatment of a plot of Equation 27 for this data yields \(R^* = 1.05\times10^{-5}R_p + 0.03\times10^{-9}\). The transfer constant for chloroform-\(^{14}\)C is then 4.8\(\times10^{-5}\).
Figure 3. Graph of $R^*$ vs. $R_p$ for the AIBN Initiated Polymerization of Styrene at 60° in the Presence of Chloroform-14C
Table 10. The Thermal Polymerization of Styrene at 60° in the Presence of Chloroform

<table>
<thead>
<tr>
<th>Run</th>
<th>[S]/[M]</th>
<th>[n]a</th>
<th>1/ P x 10^4b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>3.5423</td>
<td>1.101</td>
</tr>
<tr>
<td>2</td>
<td>0.183</td>
<td>3.4512</td>
<td>1.141</td>
</tr>
<tr>
<td>3</td>
<td>0.392</td>
<td>3.1791</td>
<td>1.277</td>
</tr>
<tr>
<td>4</td>
<td>0.555</td>
<td>3.0608</td>
<td>1.345</td>
</tr>
<tr>
<td>5</td>
<td>0.633</td>
<td>2.8914</td>
<td>1.454</td>
</tr>
<tr>
<td>6</td>
<td>0.739</td>
<td>2.8867</td>
<td>1.458</td>
</tr>
<tr>
<td>7</td>
<td>0.983</td>
<td>2.7940</td>
<td>1.524</td>
</tr>
<tr>
<td>8</td>
<td>1.188</td>
<td>2.6567</td>
<td>1.633</td>
</tr>
<tr>
<td>9</td>
<td>1.478</td>
<td>2.4928</td>
<td>1.781</td>
</tr>
</tbody>
</table>

a) Calculated using the Huggins relation, Equation 20.
b) Calculated by Equation 21.
c) A least square plot of Equation 18 for these data yields 1/ P = 4.64 x 10^-5 [S]/[M] + 1.096 x 10^-4. Therefore, the transfer constant for chloroform is 4.64 x 10^-5.
Figure 4. Graph of $1/ \bar{P}$ vs. $[S]/[M]$ for the Thermal Polymerization of Styrene at 60° in the Presence of Chloroform

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Table 11. The Thermal Polymerization of Styrene at 60° in the Presence of Chloroform-^2\text{H}

<table>
<thead>
<tr>
<th>Run</th>
<th>$[S]/[M]$</th>
<th>$[n]^a$</th>
<th>$1/\bar{P} \times 10^4^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>3.5171</td>
<td>1.112</td>
</tr>
<tr>
<td>2</td>
<td>0.181</td>
<td>3.5101</td>
<td>1.115</td>
</tr>
<tr>
<td>3</td>
<td>0.364</td>
<td>3.3921</td>
<td>1.168</td>
</tr>
<tr>
<td>4</td>
<td>0.417</td>
<td>3.3806</td>
<td>1.174</td>
</tr>
<tr>
<td>5</td>
<td>0.635</td>
<td>3.3613</td>
<td>1.183</td>
</tr>
<tr>
<td>6</td>
<td>0.747</td>
<td>3.3408</td>
<td>1.193</td>
</tr>
<tr>
<td>7</td>
<td>0.984</td>
<td>3.3052</td>
<td>1.211</td>
</tr>
<tr>
<td>8</td>
<td>1.469</td>
<td>3.1790</td>
<td>1.277</td>
</tr>
</tbody>
</table>

a) Calculated using the Huggins relation, Equation 20.
b) Calculated by Equation 21.
c) A least square plot of Equation 18 for these data yields $1/\bar{P} = 1.10 \times 10^{-5} [S]/[M] + 1.113 \times 10^{-4}$. Therefore, the transfer constant for chloroform-^2\text{H} is $1.10 \times 10^{-5}$.
Figure 5. Graph of $1/\bar{P}$ vs. $[S]/[M]$ for the Thermal Polymerization of Styrene at 60° in the Presence of Chloroform-$^2$H.

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The Transfer Constant of AIBN and Related Compounds

Chain transfer to initiator is depicted by Reactions 22 and 23.

\[
\begin{align*}
M^* + I & \rightarrow P + I! \\
I! + M & \rightarrow M^* \\
\end{align*}
\]

Equations 22 and 23

If the initiator is labelled, and the whole initiator molecule is incorporated into the polymer by Reactions 22 and 23, then a plot of the rate of incorporation of activity versus the rate of polymerization, Equation 26, will yield the transfer constant and the decomposition rate constant for the initiator.

The results for the polymerization of styrene at 60° initiated by 2,2'-azo-bis-isobutryronitrile-^3H are presented in Tables 12 and 13, and Figure 6. The value obtained for the transfer constant, \( C = k_{tr} / k_p \), was 1.7 x 10^{-2} and the value for \( k_d \) was 5.7 x 10^{-6}.

The most interesting aspect of these results is the quite high value for the transfer constant of AIBN. This will be discussed later.

The value of \( k_d \), 5.7 x 10^{-6}, obtained here is somewhat lower than the value of 6.4 x 10^{-6} obtained by Bevington^5; however, the latter value could be high due to the fact that no induced decomposition was found. If Bevington had found induced decomposition,
the plot of Equation 26, for his data, would have given a line with a slope larger than zero. This would result in a lower intercept, and, therefore, a lower value for $k_f$. The fact that these two values do not agree is not of much concern. It is known that the values of both $k_d$ and $f$ vary, sometimes quite widely; they depend on the conditions under which the decomposition of AIBN is carried out and the method used for determining $k_d$.

Arnett and Petersen\textsuperscript{54,55} have made a study of the efficiency of AIBN in the polymerization of various monomers. The monomers used and the efficiencies, $f$, determined were: methyl methacrylate, 0.52; styrene, 0.80; acrylonitrile, 1.00; vinyl acetate, 0.68-0.83; vinyl chloride, 0.50. As can be seen, these values vary over quite a large range.

The values obtained for the decomposition rate constant, $k_d$, of AIBN also vary quite widely and depend on the conditions under which the decomposition is carried out. Some of the literature values are listed in Table 14. As can be seen, the values at 60\degree vary over a three-fold range, while the values at 50\degree vary over a two-fold range.

Values of $k_d f$ for AIBN in styrene polymerizations at 60\degree include the following values: 8.52x10^{-6} from dead-end polymerization studies,\textsuperscript{56} 6.7x10^{-6} and 7.8 x 10^{-6} from dependence on the square root of the initiator concentration,\textsuperscript{57,2} and 6.4 x 10^{-6}
from determinations using labelled AIBN. The results here and the latter result by Bevington using labelled AIBN seem to be somewhat lower than values obtained by other methods. Although the value obtained here is lower than the rest, the method may give slightly different answers and as was stated earlier, Bevington's results could easily be high.

As was previously stated, the value obtained for the transfer constant was surprisingly high. It has been widely believed that azo compounds, and particularly AIBN, are not subject to induced decomposition. The value obtained for the transfer constant of AIBN was $1.7 \times 10^{-2}$. This number is quite large in comparison with the majority of transfer constants in the literature. It is apparent that some explanation must be made as to why this large transfer constant had not been previously measured, and why AIBN would be so susceptible to induced decomposition.

To try to ascertain what value for the transfer constant of AIBN would be expected, a study of model compounds was made. Tetramethylsuccinodinitrile is identical to AIBN except that the azo linkage is missing. This compound along with trimethylacetonitrile ought to give a reasonable estimate of the rate of hydrogen abstraction from AIBN.

The results for the thermal polymerization of styrene at $60^\circ$ in the presence of tetramethylsuccinodinitrile are presented in Table 15 and Figure 7. The transfer constant obtained from a plot of Equation 18 was $3.7 \times 10^{-5}$. 

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The results for the thermal polymerization of styrene at 60° in the presence of trimethylacetonitrile are presented in Table 16 and Figure 8. The transfer constant obtained from a plot of Equation 18 was 3.8 x 10^-5.

From the data for the transfer constants of tetramethylsuccinodinitrile and trimethylacetonitrile, it would seem logical that AIBN should have a transfer constant of the magnitude of 4 x 10^-5, if the transfer step simply involved hydrogen abstraction and the resulting radical re-initiated chain growth. This value is about the magnitude expected for a compound containing only primary aliphatic hydrogens.

Listed in Table 17 are literature values for transfer constants of compounds having only primary hydrogens. It is apparent from the data that compounds having only primary aliphatic hydrogens, which are not close to any activating group, exhibit transfer constants on the order of 5 x 10^-5. If there is some activating group affecting the reactivity of these hydrogens, the transfer constant may be 10^-4 or larger. n-Butyl sulfide, which has secondary hydrogens, has been added to this list for the following comparison. Secondary hydrogens are more likely to be abstracted by a radical than primary hydrogens. However, the transfer constant for t-butyl sulfide is a factor of ten larger than that for n-butyl sulfide. The proposed explanation for this enhanced rate of reaction is a synchronous beta scission accompanying hydrogen
abstraction to yield iso-butylene and the highly stable thyl radical.

If, on hydrogen abstraction from AIBN, a synchronous beta, delta scission occurs, not only would a conjugated olefin and a resonance stabilized radical be produced, but a molecule of nitrogen would be formed as well.

If this synchronous scission does occur, it could account for the factor of 400 that is apparent in the increase of rate of hydrogen abstraction over the value which would be predicted. It must be noted that Equation 26 was derived by assuming the incorporation of a complete molecule of initiator into the polymer for each transfer step. The synchronous scission mechanism would only incorporate half an initiator molecule, therefore, half of the activity would be lost for each transfer step, and the value of \( C = 1.7 \times 10^{-2} \) would be low by one-half. The true transfer constant would then be \( 3.4 \times 10^{-2} \), for a synchronous scission mechanism.

The tracer method for the determination of the transfer constant of an initiator is probably the most accurate, and certainly the most sensitive. However, it must be pointed out that this method has its limitations. When Bevington suggested this method, he successfully measured the transfer constant of a substituted...
benzoyl peroxide, which was determined to be 1.34. In the same work, Bevington tried to measure the transfer constant of AIBN. He reported that there was apparently no transfer to AIBN. The line corresponding to a transfer constant for AIBN of $10^{-4}$ is included in Figure 6. This line has essentially no slope. It is evident that under these conditions, the method is not sensitive enough to be able to detect a transfer constant for AIBN on the order of $10^{-4}$ or smaller. The probable reason why Bevington was not able to detect a transfer constant for AIBN under these conditions was the fact that his range of $R_p$ was between $0.6 \times 10^{-4}$ and $0.8 \times 10^{-4}$. Even with the large transfer constant found in this study, this would be too small a range of $R_p$ to accurately determine if transfer did occur.

From Equation 26, the slope is equal to the transfer constant times the initiator-to-monomer ratio. Therefore, if one used a higher concentration of initiator, the slope of the plot of Equation 26 could be increased, and therefore, the accuracy of the results could be increased as well. This method of increasing the accuracy of the results has its limitations, as will be explained.

Okamura\textsuperscript{2} has studied the effect on the inverse of the degree of polymerization, $1/P$, of styrene, initiated by AIBN, with increasing $R_p$. These data, along with similar data obtained in this study, are presented in Table 18 and Figure 9. Primary radical
termination becomes an important factor at or above $R_p$ of about $1.7 \times 10^{-4}$. This corresponds to a molarity of AIBN of slightly more than $4 \times 10^{-2}$. The molarity of labelled AIBN used in the tracer study was $4 \times 10^{-3}$. Therefore, the concentrations of AIBN could be increased only very slightly since the concentration of labelled AIBN must be low enough to allow the addition of inactive initiator and leave a sufficiently large range of $R_p$ to be able to determine the transfer constant. That is, $R_p$ values above $1.7 \times 10^{-4}$ could not be used for the determination of the transfer constant, as primary radical termination becomes important.

Another explanation for the observed high transfer constant of AIBN becomes apparent when considering Figure 10. Here is plotted the data of Okamura, Table 18, for $1/R_p$ dependence on $R_p$, along with the same data as obtained in this study for labelled AIBN, Table 13. As can be seen, the straight line portion for the labelled AIBN data has a somewhat higher slope than that obtained by molecular weight studies. If both sets of data are accurate, this points to the possibility that AIBN is becoming incorporated into the polymer in positions other than the end of the polymer chain. AIBN could, by this reasoning, be copolymerizing by addition through the cyano group. This would appear in a plot of Equation 26 to be transfer to AIBN, as both transfer and copolymerization follow the same kinetic dependence.

\[
\begin{align*}
M^* + I & \longrightarrow P + I! & k_{tr} & [M^*][I] \\
M + I & \longrightarrow MI^* & k_{cop} & [M^*][I]
\end{align*}
\] (22) (45)
There is no real precedent for this explanation. Transfer studies by molecular weight techniques would not show evidence of copolymerization. However, if other cyano compounds do copolymerize with styrene, the use of a labelled cyano compound to determine the transfer constant and subsequent comparison with the transfer constant obtained by molecular weight techniques would reveal if copolymerization had occurred.

Some support for the notion that nitrile containing molecules copolymerize may be found in the fact that in the determination of the transfer constant of trimethylacetonitrile, 1/\(P\) became very large quite rapidly above \([S]/[N]\) values in excess of 0.5. The explanation for this phenomena could be that addition to the cyano group could have taken place. The resulting radical might have sufficient stability to cause an increase in the rate of termination, which would lead to lower molecular weight polymer.

Johnson and Tobolsky have stated that the transfer constant of styrene of AIBN is effectively zero. However, they qualify this statement by stating that the transfer constant must be finite. Their explanation for their conclusion lies in the fact that the value of \(k_d\) is quite high for AIBN, and to be able to
determine if transfer did occur, would involve rates of polymer-
ization that would be too high to measure accurately.

Mayo, Gregg, and Matheson\textsuperscript{62} have measured the transfer con-
stant of benzoyl peroxide by a molecular weight technique. They
have presented a particularly useful graph showing how the various
termination mechanisms contribute to the overall molecular weight
of styrene polymerized at various concentrations of benzoyl per-
oxide. Their graph is reproduced in Figure 11. The same plot for
AIBN data is presented in Figure 12. These data are calculated from
an extension of Equation 17, which is modified only to the extent
of having a term added for transfer to monomer.

\[
\frac{1}{P} = C_m + C_I \frac{[S]}{[M]} + \frac{\delta^2}{[M]^2} \frac{R}{p}
\]  \hspace{1cm} (46)

Where $C_m$ is the transfer constant for monomer, and $C_I$ is the transfer constant for initiator. The data for the plot of AIBN work in
Figure 12 is taken from the data of Okamura\textsuperscript{2} and the molecular
weight work of this study. The data were found to fit the follow-
ing relations.

\[ 1/P \times 10^3 = 0.8432 \times 10^4 \frac{R}{p} + 7.8 \times 10^{-6} \]  \hspace{1cm} (47)

\[ R \times 10^4 = 0.788[I]^{1/2} \times 10 \]  \hspace{1cm} (48)

The values for $1/P$ were calculated for different initiator con-
centrations from these equations.
As is evident from a comparison of these plots for benzoyl peroxide and AIBN, the relative amount of termination due to transfer to initiator is much larger for benzoyl peroxide. Another factor becomes obvious if one assumes that primary radical termination begins at the same value of $R_p$ for every initiator. The molarity of AIBN at which primary radical termination becomes operative is $4 \times 10^{-2}$ m. Using the value for $k_{df}$ for benzoyl peroxide of $2.0 \times 10^{-6}$, as determined by Bevington, primary radical termination does not begin until molarities of benzoyl peroxide are reached that are greater than $1.3 \times 10^{-1}$.

In Figure 13 is presented the extended plot of Figure 12 showing the relative amount of termination due to primary radical termination. The values determined for primary radical termination are the difference between the calculated $1/\bar{P}_p$ and the experimentally determined values of Okamura. It can be seen that primary radical termination accounts for a relatively high portion of the termination above AIBN molarities of $10^{-1}$.

Another approach to the determination of the transfer constant of AIBN was tried. It was felt that if one would try to measure the transfer constant at a lower temperature, the decomposition rate constant would be lower and transfer might account for a larger percentage of the activity incorporated into the polymer.

The data for the polymerization of styrene at $30^\circ$ in the presence of $2,2'$-azo-bis-isobutyronitrile-3H is presented in Table 19.
As can be seen, the data are very imprecise, and no conclusions could be drawn from this portion of the study. The values are probably incorrect due to the method of purification of the polymer.

In summary, then, we see that the problem of accurately measuring the transfer constant of AIBN is limited by the fact that the value of $k_f$ is quite high, and the relative amount of termination due to transfer is small in comparison with initiation. The problem is also increased by the fact that primary radical termination becomes an important reaction at relatively low concentrations of AIBN.

In conclusion, one can safely assume that the transfer constant of AIBN is certainly no lower than $4 \times 10^{-5}$ and could even be as high as $3.4 \times 10^{-2}$. 

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Table 12. The Polymerization of Styrene at 60° Initiated by 2,2'-Azo-bis-isobutyronitrile-$^3_H$

<table>
<thead>
<tr>
<th>[M]$^a$</th>
<th>[I$^*$$]_a,b$</th>
<th>g Polymer</th>
<th>R x10$^4c$</th>
<th>dpm in Polymer</th>
<th>R$^4x10^8d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.91</td>
<td>3.93</td>
<td>0.8144</td>
<td>0.44</td>
<td>12,832</td>
<td>2.23</td>
</tr>
<tr>
<td>7.90</td>
<td>3.92</td>
<td>0.8030</td>
<td>0.87</td>
<td>6,538</td>
<td>2.28</td>
</tr>
<tr>
<td>7.89</td>
<td>3.92</td>
<td>0.9177</td>
<td>1.00</td>
<td>6,454</td>
<td>2.25</td>
</tr>
<tr>
<td>7.87</td>
<td>3.91</td>
<td>0.8870</td>
<td>1.45</td>
<td>4,369</td>
<td>2.29</td>
</tr>
<tr>
<td>7.83</td>
<td>3.89</td>
<td>0.8607</td>
<td>1.87</td>
<td>3,319</td>
<td>2.32</td>
</tr>
<tr>
<td>7.76</td>
<td>3.85</td>
<td>0.8761</td>
<td>2.38</td>
<td>2,760</td>
<td>2.41</td>
</tr>
<tr>
<td>7.72</td>
<td>3.83</td>
<td>0.8416</td>
<td>2.74</td>
<td>2,293</td>
<td>2.40</td>
</tr>
<tr>
<td>7.62</td>
<td>3.78</td>
<td>0.8915</td>
<td>3.33</td>
<td>2,093</td>
<td>2.51</td>
</tr>
<tr>
<td>7.52</td>
<td>3.73</td>
<td>0.8833</td>
<td>3.78</td>
<td>1,829</td>
<td>2.52</td>
</tr>
</tbody>
</table>

a) Molarities are calculated at half reaction.

b) The specific activity of the AIBN-$^3_H$ is $3.239x10^9$ dpm/mole.

\[
[M]/[I^*] = 2.013x10^3.
\]

c) Calculated by Equation 28.

d) Calculated by Equation 29.
Table 13. Calculation of the Molecular Weight of the Polymer Formed in the Polymerization of Styrene at 60° Initiated by 2,2'-Azo-bis-isobutynitrile-^3H

<table>
<thead>
<tr>
<th>Secx10^3</th>
<th>Vol. ml^a</th>
<th>[I]^a Total</th>
<th>Total dpm/mole</th>
<th>Fx10^-2c</th>
<th>1/Fx10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.48</td>
<td>8.271</td>
<td>3.93x10^-3</td>
<td>3.239x10^9</td>
<td>19.74</td>
<td>0.506</td>
</tr>
<tr>
<td>10.68</td>
<td>8.289</td>
<td>1.56x10^-2</td>
<td>8.128x10^8</td>
<td>9.59</td>
<td>1.043</td>
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<tr>
<td>10.68</td>
<td>8.292</td>
<td>1.78x10^-2</td>
<td>7.154x10^8</td>
<td>9.77</td>
<td>1.022</td>
</tr>
<tr>
<td>7.08</td>
<td>8.320</td>
<td>3.59x10^-2</td>
<td>3.536x10^8</td>
<td>6.89</td>
<td>1.451</td>
</tr>
<tr>
<td>5.28</td>
<td>8.364</td>
<td>6.48x10^-2</td>
<td>1.961x10^8</td>
<td>4.88</td>
<td>2.049</td>
</tr>
<tr>
<td>4.20</td>
<td>8.417</td>
<td>9.98x10^-2</td>
<td>1.274x10^8</td>
<td>3.88</td>
<td>2.577</td>
</tr>
<tr>
<td>3.48</td>
<td>8.475</td>
<td>1.38x10^-1</td>
<td>1.182x10^8</td>
<td>4.13</td>
<td>2.421</td>
</tr>
<tr>
<td>3.00</td>
<td>8.582</td>
<td>2.09x10^-1</td>
<td>6.096x10^7</td>
<td>2.49</td>
<td>4.016</td>
</tr>
<tr>
<td>2.58</td>
<td>8.687</td>
<td>2.78x10^-1</td>
<td>4.577x10^7</td>
<td>2.12</td>
<td>4.717</td>
</tr>
</tbody>
</table>

a) Calculated at half reaction.

b) Calculated by dividing the dpm, a constant, in each sample by the total moles of AIBN present.

c) Calculated by means of Equation 30.
Figure 6. Graph of R* vs. R_p for the Polymerization of Styrene at 60° Initiated by AIBN-^3H.

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Table 14. Literature Values of the Decomposition Rate Constant for 2,2'-Azo-bis-isobutyronitrile

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>$k_d \times 10^6$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>50</td>
<td>1.50</td>
<td>26</td>
</tr>
<tr>
<td>Dioxane</td>
<td>50</td>
<td>1.54</td>
<td>26</td>
</tr>
<tr>
<td>Butanone</td>
<td>50</td>
<td>2.06</td>
<td>26</td>
</tr>
<tr>
<td>Pyridine</td>
<td>50</td>
<td>2.06</td>
<td>26</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>50</td>
<td>2.06</td>
<td>26</td>
</tr>
<tr>
<td>Benzene</td>
<td>50</td>
<td>2.18</td>
<td>26</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>50</td>
<td>2.61</td>
<td>26</td>
</tr>
<tr>
<td>Benzene</td>
<td>60</td>
<td>8.45</td>
<td>64</td>
</tr>
<tr>
<td>Toluene</td>
<td>60</td>
<td>9.15</td>
<td>65</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>60</td>
<td>4.00</td>
<td>66</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>60</td>
<td>9.36</td>
<td>66</td>
</tr>
<tr>
<td>Benzene</td>
<td>60</td>
<td>11.6</td>
<td>66</td>
</tr>
</tbody>
</table>

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Table 15. The Thermal Polymerization of Styrene at 60° in the Presence of Tetramethylsuccinodinitrile

<table>
<thead>
<tr>
<th>Run</th>
<th>[S]/[M]</th>
<th>([\eta]^a)</th>
<th>(1/\bar{P} \times 10^{-4})</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>3.6567</td>
<td>1.054</td>
</tr>
<tr>
<td>2</td>
<td>0.069</td>
<td>3.5660</td>
<td>1.087</td>
</tr>
<tr>
<td>3</td>
<td>0.133</td>
<td>3.5020</td>
<td>1.118</td>
</tr>
<tr>
<td>4</td>
<td>0.294</td>
<td>3.3698</td>
<td>1.179</td>
</tr>
<tr>
<td>5</td>
<td>0.388</td>
<td>3.3038</td>
<td>1.211</td>
</tr>
<tr>
<td>6</td>
<td>0.575</td>
<td>3.1910</td>
<td>1.266</td>
</tr>
</tbody>
</table>

a) Calculated using the Huggins relation, Equation 20.
b) Calculated by Equation 21.
c) A least square plot of Equation 18 for these data yields \(1/\bar{P} = 3.68 \times 10^{-5} [S]/[M] + 1.063 \times 10^{-4}\). Therefore, the transfer constant for tetramethylsuccinodinitrile is \(3.68 \times 10^{-5}\).
Figure 7. Graph of $1/P$ vs. $[S]/[M]$ for the Thermal Polymerization of Styrene at $60^\circ$ in the presence of Tetramethylsuccinonitrile.
Table 16. The Polymerization of Styrene at 60° in the Presence of Trimethylacetonitrile

<table>
<thead>
<tr>
<th>Run</th>
<th>[S]/[M]</th>
<th>([n]^{a})</th>
<th>1/(P\times10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>3.5101</td>
<td>1.115</td>
</tr>
<tr>
<td>2</td>
<td>0.039</td>
<td>3.4962</td>
<td>1.121</td>
</tr>
<tr>
<td>3</td>
<td>0.080</td>
<td>3.3725</td>
<td>1.178</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>3.3464</td>
<td>1.190</td>
</tr>
<tr>
<td>5</td>
<td>0.175</td>
<td>3.2862</td>
<td>1.214</td>
</tr>
<tr>
<td>6</td>
<td>0.226</td>
<td>3.2988</td>
<td>1.220</td>
</tr>
<tr>
<td>7</td>
<td>0.282</td>
<td>3.2346</td>
<td>1.247</td>
</tr>
<tr>
<td>8</td>
<td>0.357</td>
<td>3.2927</td>
<td>1.240</td>
</tr>
</tbody>
</table>

a) Calculated using the Huggins relation, Equation 20.
b) Calculated by Equation 21.
c) A least square plot of Equation 18 for these data yields 1/\(P\) = 3.82x10\(^{-5}\) [S]/[M] + 1.130x10\(^{-4}\). Therefore, the transfer constant for trimethylacetonitrile is 3.82x10\(^{-5}\).
Figure 8. Graph of $1/P$ vs. $S/M$ for the Thermal polymerization of Styrene at $60^\circ$ in the Presence of Trimethylacetonitrile
Table 17. Chain Transfer Constants for the Polystyryl Radical at 60° on Various Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$C \times 10^4$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethylsuccinodinitrile</td>
<td>0.37</td>
<td>This work</td>
</tr>
<tr>
<td>Trimethylacetonitrile</td>
<td>0.38</td>
<td>This work</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.44</td>
<td>67</td>
</tr>
<tr>
<td>t-Butylbenzene</td>
<td>0.06</td>
<td>68</td>
</tr>
<tr>
<td>Methyl Disulfide</td>
<td>94.0</td>
<td>69</td>
</tr>
<tr>
<td>t-Butyl Disulfide</td>
<td>1.42</td>
<td>69</td>
</tr>
<tr>
<td>n-Butyl Sulfide</td>
<td>21.8</td>
<td>69</td>
</tr>
<tr>
<td>t-Butyl Sulfide</td>
<td>250.0</td>
<td>69</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>0.43</td>
<td>69</td>
</tr>
<tr>
<td>t-Butyl peroxide</td>
<td>8.6</td>
<td>20</td>
</tr>
</tbody>
</table>

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Table 18. The Molecular Weight of the Polymer Formed in the AIBN-Initiated Polymerization of Styrene at 60°

<table>
<thead>
<tr>
<th>( \bar{M}_n \times 10^4 )</th>
<th>( 1/ \bar{M}_n \times 10^3 )</th>
<th>( \bar{M}_n \times 10^4 )</th>
<th>( 1/ \bar{M}_n \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.46</td>
<td>0.450</td>
<td>0.44</td>
<td>0.432</td>
</tr>
<tr>
<td>0.70</td>
<td>0.624</td>
<td>0.77</td>
<td>0.703</td>
</tr>
<tr>
<td>0.94</td>
<td>0.860</td>
<td>0.98</td>
<td>0.863</td>
</tr>
<tr>
<td>1.18</td>
<td>1.087</td>
<td>1.26</td>
<td>1.144</td>
</tr>
<tr>
<td>1.40</td>
<td>1.300</td>
<td>1.57</td>
<td>1.433</td>
</tr>
<tr>
<td>1.82</td>
<td>1.727</td>
<td>1.73</td>
<td>1.610</td>
</tr>
<tr>
<td>2.06</td>
<td>2.083</td>
<td>1.96</td>
<td>1.852</td>
</tr>
<tr>
<td>2.46</td>
<td>2.564</td>
<td>2.15</td>
<td>2.016</td>
</tr>
<tr>
<td>2.67</td>
<td>2.899</td>
<td>2.29</td>
<td>2.257</td>
</tr>
<tr>
<td>2.79</td>
<td>3.086</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Data from Reference 2.

b) Data from this work using viscosity molecular weight.
Figure 9. The Molecular Weight of the Polymer Formed in the AIBN-Initiated Polymerization of Styrene at 60°. O Data from Reference 2. △ $\bar{P}$ Calculated from Viscosity Data in this Work.
Figure 10. The Molecular Weight of the Polymer Formed in the AIBN-Initiated Polymerization of Styrene at 60°. ○ Data from Reference 2. △ Tracer Data for This Work

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Figure 11. Graph of $1/P$ vs. $[I]$ for the Polymerization of Styrene at 60° Initiated by Benzoyl Peroxide. Data taken from Reference 62 using $C_i = 5.6 \times 10^{-2}$ and $C_m$, Transfer to Monomer, = $6 \times 10^{-5}$
Figure 12. Graph of $1/\bar{P}$ vs. $[I]$ for the Polymerization of Styrene at $60^\circ$ Initiated by AIBN. Calculated Using $C_i = 1.7 \times 10^{-2}$ and $C_m = 6 \times 10^{-5}$.
Figure 13. Graph of $1/P$ vs. $[I]$ for the Polymerization of Styrene at 60° Initiated by AIBN Calculated Using $C_i = 1.7 \times 10^{-2}$ and $C_m = 6 \times 10^{-5}$. Included Data for Primary Radical Termination, PRT.

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Table 19. The Polymerization of Styrene at 30° in the Presence of 2,2'-Azo-bis-isobutyronitrile-3H

<table>
<thead>
<tr>
<th>Run</th>
<th>[IPP] x10³</th>
<th>g Polymer</th>
<th>R x10⁵</th>
<th>dpm in Polymer x10⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td></td>
<td>2,075</td>
</tr>
<tr>
<td>1</td>
<td>0.12</td>
<td>0.7125</td>
<td>0.99</td>
<td>160,175</td>
</tr>
<tr>
<td>2</td>
<td>0.48</td>
<td>0.5916</td>
<td>1.64</td>
<td>74,948</td>
</tr>
<tr>
<td>3</td>
<td>1.93</td>
<td>0.4575</td>
<td>2.54</td>
<td>28,222</td>
</tr>
<tr>
<td>4</td>
<td>3.62</td>
<td>0.4570</td>
<td>3.90</td>
<td>22,377</td>
</tr>
</tbody>
</table>

a) The molarity of AIBN is 7.70 x 10⁻².

b) The specific activity of the AIBN-3H is 8.862 x 10¹⁰ dpm/mole.
The Determination of the Relative Rates of Addition of Phenyl Radicals to Polymerizable Olefins

When phenylazotriphenylmethane, PAT, is decomposed in solutions containing varying ratios of a monomer and heptanethiol-$^3$H, the phenyl radical formed by decomposition of PAT will partition itself between Reactions 34 and 35.

\[ \phi^* + M \rightarrow \phi M^* \quad k_1[\phi^*][M] \quad (34) \]
\[ \phi^* + RSH* \rightarrow \phi H^* \quad k_T[\phi^*][RSH] \quad (35) \]

The amount of reaction proceeding by way of Reaction 35 will depend on the monomer-to-heptanethiol ratio and the reactivity of the monomer. The rate of Reaction 35 was followed by measuring the rate of incorporation of activity, $R^*$, into the benzene that was formed. This was converted to the rate of formation of benzene, $R_f$, by multiplying the value obtained for $R^*$ by the tritium isotope effect, $k_H/k_T$, for hydrogen abstraction from heptanethiol by the phenyl radical.

\[ R_f = k_H[\phi^*][RSH] = k_H/k_T R^* \quad (37) \]

The tritium isotope effect was determined by comparing the relative amounts of benzene and benzene-$^3$H formed when varying amounts of PAT were decomposed in heptanethiol and heptanethiol-$^3$H.
The data are presented in Table 20 and Figure 14. The tritium isotope effect for the phenyl radical abstracting hydrogen from heptanethiol was determined to be 2.0.

Equation 40:

\[
\frac{1}{R_f} = \frac{k_1[M]}{k_H[RSH] k_d f[I]_0 \int_0^t e^{-kd t} dt} + \frac{1}{k_d f[I]_0 \int_0^t e^{-kd t} dt}
\]

was derived to enable one to determine the relative reactivity of different monomers with the phenyl radical when PAT is decomposed in solutions containing varying ratios of the monomer and heptanethiol-\(^3\)H. By plotting the inverse of the rate of formation of benzene against the monomer-to-heptanethiol ratio for a particular monomer a straight line was obtained which fitted the kinetic relationship described by Equation 40. The slope of this plot should be equal to \(k_1/k_H k_d f[I]\), while the intercept should be equal to \(1/k_d f[I]\). ([I] will be used in the discussion and results for the sake of brevity.) By comparing the slopes of the plots of Equation 40 for different monomers one should obtain the relative rate of addition of phenyl radicals to the monomers. The validity of this comparison of slopes depends on whether or not the value of \(k_d f[I]\) remains constant from one monomer system to the next.

As was discussed previously, pages 19-21, it is known that the value of \(k_d f\) for various initiators will vary depending on the conditions under which the decomposition is carried out. The
conclusion was reached that, in this study, $k_{df}$ would have to be assumed to be a constant from one system to the next.

The concentration of PAT, $[I]$, varies from the start to the finish of the reaction. $[I]$ was replaced in Equation 40 by the variable time, which may be held constant. (For brevity, the results are reported in terms of $[I]$ as in Equation 39). To test the validity of Equation 40, the following experiments were run.

It was reasoned that the relative values obtained from the slopes of plots of Equation 40, from data obtained using two different reaction times for a given monomer, should be equal to the relative values obtained, in the same fashion, for a second monomer. Styrene and $\alpha$-methylstyrene were chosen to run this test. The data for styrene are presented in Table 21 and Figures 15 and 18. The data for $\alpha$-methylstyrene are presented in Table 22 and Figures 16 and 19. The slopes of the lines obtained from a plot of Equation 40, and the reaction times were:

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Slope</th>
<th>Sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene</td>
<td>13.46x10^4</td>
<td>1.2x10^3</td>
</tr>
<tr>
<td></td>
<td>16.90x10^4</td>
<td>2.4x10^3</td>
</tr>
<tr>
<td>$\alpha$-methylstyrene</td>
<td>16.64x10^4</td>
<td>1.2x10^3</td>
</tr>
<tr>
<td></td>
<td>20.97x10^4</td>
<td>2.4x10^3</td>
</tr>
</tbody>
</table>
Comparison of the two slopes for styrene and the two slopes for α-methylstyrene yield relative values of 1.255 and 1.260 respectively. As is evident, the agreement is quite good.

To further test the derived equations, the slope of a plot of Equation 40 was determined for styrene using two different initial concentrations of PAT and the same reaction time. These results are presented in Table 21 and Figures 17 and 18. The slopes obtained from a plot of Equation 40, and the initial Molarities of PAT were: $1.346 \times 10^4$, $4.16 \times 10^{-3}$; $6.77 \times 10^4$, $8.32 \times 10^{-3}$. The ratio of the two slopes is 0.503. This number is what would be expected, as one would expect to double the rate of formation of benzene by doubling the initiator concentration. The inverse of the rate of formation of benzene for twice the initial initiator concentration would then be one-half. It would also be expected that the rate of formation of benzene would not be quite twice the value obtained for an initiator concentration that is smaller by a factor of two. This is evident from Figure 14, which shows that as the initial concentration of PAT is increased, the total yield of phenyl radicals drops. The value of 0.503 is consistent with this prediction.
It would seem that if one uses the same initial concentration of PAT and the same reaction time for each sample, the comparison of the slopes obtained from a plot of Equation 40 for a series of monomers would give the relative reactivity of each monomer towards the phenyl radical. The only uncertainty in the method would arise from a variation in the value of $k_d^f$.

The data for the relative reactivity of the monomers used in this study towards the phenyl radical are presented in Tables 21 through 29 and in Figures 18 through 26. In all cases, the initial molarity of PAT was $4.16 \times 10^{-3}$ and the reaction time was $1.2 \times 10^3$ sec. All determinations were made at 60°. The results are tabulated in Table 30. The values for the slopes of Equation 40 will be discussed in detail later.

On inspection of the values obtained for the intercepts from plots of Equation 40 one immediately notices that the values vary over quite a large range. It is felt that these values are imprecise for the following reasons. The values obtained for the intercepts are relatively small. The determination of the value of an intercept is subject to a larger amount of uncertainty than is the determination of a slope, and the error is magnified as the intercept approaches zero. From Equation 40 one sees that $k_i/k_H$ may be obtained explicitly by dividing the slope by the intercept. This treatment was not used since the values of $k_d^f$ that were obtained from the intercept are imprecise. In fact, this treatment yields values of $k_i/k_H$ which do not correlate well with methyl affinities or other similar parameters (to be discussed in the following pages).
Among the more striking developments in physical organic chemistry is the correlation of rate constants. According to the relation:

\[ \Delta F^0 = -RT \ln K \]  

the equilibrium constant for a reaction depends only on the difference in standard free energies of the reactants and products. According to transition state theory, the activated complex is considered to be in equilibrium with the reactants. Therefore, the rate constant depends similarly on the free-energy difference between the reactants and the activated complex. Thus, estimates of rate constants are equivalent to estimates of free-energy differences between various species.

The utility of Equation 49 can be seen to apply to the data obtained here in the following fashion. If the log of the relative rates of addition of one species to a series of substrates is plotted against the log of the relative rates of addition of a second species to the same set of substrates, the slope of the line obtained will be a measure of the relative selectivity of the two species in question in additions to these substrates. A statistical factor, n, must be included in the data for monomers that have more than one equally probable site of attack. Thus, for instance, the relative rate of addition of a particular species to maleic anhydride would have to be divided by two.
As seen in the work of Szwarc and co-workers, \(^6\) a plot of the relative rates of addition of methyl radicals to monomers is compared with the inverse of the copolymerization reactivity ratio, \(r^1\), which is the relative rate of addition, of the polystyryl radical to the same series of monomers. These data are reproduced in Table 31 and Figure 27. The slope obtained from the plot of Figure 27 is then a measure of the relative selectivity of these two radicals in additions to monomers. From this plot one finds that the polystyryl radical is 1.25 times more selective than the methyl radical in additions to monomers.

The data obtained here for the relative rates of addition of the phenyl radical to monomers is compared to the relative rates of addition of the polystyryl radical, Figure 28, and the methyl radical, Figure 29 to the same set of monomers. The slopes of the lines obtained from this treatment of the data shows that the polystyryl radical is 2.37 times more selective, and the methyl radical is 1.73 times more selective than the phenyl radical in additions to monomers.

The apparent low selectivity of the phenyl radical might at first seem somewhat surprising. Trotman-Dickinson\(^7\) presents data for the addition of methyl, ethyl, and phenyl radicals to aromatic compounds. These data show that the phenyl radical is only slightly less selective than the methyl and ethyl radicals in additions to aromatic compounds. However, this work was based on only three monomers.
To attempt to rationalize the relative unselectivity of the phenyl radical found in this study, one can cite the following examples of the comparative unselectivity of the phenyl radical in hydrogen abstraction reactions.

In recent work, the tritium isotope effects for abstraction of hydrogen from thiols by different radicals have been measured. In this study, the tritium isotope effect on hydrogen abstraction from heptanethiol by the phenyl radical has been determined to be 2.0. The tritium isotope effect on hydrogen abstraction from heptanethiol by the triphenylmethyl radical has been determined to be 7.6. Wall and Brown have determined the deuterium isotope effect on hydrogen abstraction from n-butanesulhol by the polystyryl radical. Their value of 4.0 for $k_H/k_D$ corresponds to a tritium isotope effect of 7.4. As is evident, the phenyl radical, when compared to the polystyryl or triphenylmethyl radicals, is quite unselective in the abstraction of hydrogen in preference to tritium from thiols.

Tabulated in Table 32 are the data for the relative rates of abstraction of benzylic hydrogens from toluene, ethylbenzene and cumene by the phenyl, methyl and polystyryl radicals. It is again quite evident that the phenyl radical is quite unselective in comparison with other radicals in hydrogen abstraction reactions.
From bond dissociation energies, one can also rationalize the relative selectivities demonstrated by the phenyl, methyl, and polystyryl radicals. (The assumption is made that the bond dissociation energy for polystyrene is of the order of magnitude of the bond dissociation energy of toluene.) The bond dissociation energies for the relevant species (kcal./mole at 25°) are:

<table>
<thead>
<tr>
<th>R in R-H</th>
<th>D(R-H)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CH₂-</td>
<td>85</td>
<td>93</td>
</tr>
<tr>
<td>CH₃-</td>
<td>104</td>
<td>94</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>112</td>
<td>95</td>
</tr>
</tbody>
</table>

If one assumes that the energy gained from additions to olefins parallels the energy differences in the above dissociation energies, then it becomes apparent that the order of selectivity in addition reactions should decrease in the order polystyryl, methyl, and phenyl.

An additional note as to the accuracy of the results obtained here might be seen in the following comparisons. In Table 33 are presented data for copolymerization reactivity ratios for the poly (methyl methacrylate) radical. These are compared to the similar reactivity ratios for the polystyryl radical in Figure 30. As can be seen, the results do not give a good fit in the previously described log-log plot. Also, Table 34 and Figure 31 present the
relative rates of addition of benzoyloxy radicals to phenyl substituted ethylenes as compared to the methyl radical. A comparison of Figures 30 and 31 with the data obtained here, Figures 28 and 29, show that the accuracy of this work seems to be quite good.

In conclusion, one can say that the phenyl radical, in comparison to the methyl and polystyryl radicals, seems to be quite unselective in additions to polymerizable olefins.
Table 20. The Decomposition of PAT at 60° in Heptanethiol and Heptanethiol-H³

<table>
<thead>
<tr>
<th>Isotope and Run</th>
<th>[PAT]x10²</th>
<th>[OH]x10²</th>
<th>dpm</th>
<th>[OH⁺]x10²</th>
</tr>
</thead>
<tbody>
<tr>
<td>³H-1</td>
<td>0.40</td>
<td></td>
<td>32,230⁹</td>
<td>0.19</td>
</tr>
<tr>
<td>³H-2</td>
<td>0.80</td>
<td></td>
<td>61,333⁹</td>
<td>0.36</td>
</tr>
<tr>
<td>³H-3</td>
<td>1.81</td>
<td></td>
<td>148,882⁸</td>
<td>0.79</td>
</tr>
<tr>
<td>³H-4</td>
<td>2.43</td>
<td></td>
<td>179,767⁸</td>
<td>0.96</td>
</tr>
<tr>
<td>³H-5</td>
<td>4.85</td>
<td></td>
<td>367,704⁸</td>
<td>1.96</td>
</tr>
<tr>
<td>¹H-1</td>
<td>0.83</td>
<td></td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>¹H-2</td>
<td>1.66</td>
<td></td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>¹H-3</td>
<td>1.88</td>
<td></td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>¹H-4</td>
<td>3.76</td>
<td></td>
<td>3.04</td>
<td></td>
</tr>
</tbody>
</table>

a) The specific activity of the thiol is 3.573x10¹⁰ dpm/mole.
b) The specific activity of the thiol is 3.762x10¹⁰ dpm/mole.
c) The experimentally determined tritium isotope effect is 2.0.
Figure 14. The Decomposition of PAT at 60° in Heptanethiol and Heptanethiol-3H. O for $\phi H$; $\Delta$ for $\phi H^*$. 

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Table 21. The Relative Rate of Addition of the Phenyl Radical to Styrene

<table>
<thead>
<tr>
<th>Run</th>
<th>[RSH]</th>
<th>[M]/[RSH]</th>
<th>dpm</th>
<th>Moles ( \phi_H \times 10^6 )</th>
<th>( R^2 \times 10^7 )</th>
<th>( 1/R^2 \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.135</td>
<td>57.84</td>
<td>17,984</td>
<td>0.742</td>
<td>1.189</td>
<td>8.410</td>
</tr>
<tr>
<td>2</td>
<td>0.282</td>
<td>28.01</td>
<td>33,717</td>
<td>1.392</td>
<td>2.230</td>
<td>4.484</td>
</tr>
<tr>
<td>3</td>
<td>0.332</td>
<td>23.64</td>
<td>39,329</td>
<td>1.624</td>
<td>2.603</td>
<td>3.842</td>
</tr>
<tr>
<td>4</td>
<td>0.565</td>
<td>13.34</td>
<td>61,580</td>
<td>2.542</td>
<td>4.074</td>
<td>2.456</td>
</tr>
<tr>
<td>5</td>
<td>0.664</td>
<td>11.17</td>
<td>68,574</td>
<td>2.832</td>
<td>4.538</td>
<td>2.204</td>
</tr>
<tr>
<td>6</td>
<td>1.129</td>
<td>6.01</td>
<td>109,172</td>
<td>4.508</td>
<td>7.224</td>
<td>1.384</td>
</tr>
<tr>
<td>7</td>
<td>0.121</td>
<td>67.09</td>
<td>25,055</td>
<td>1.402</td>
<td>2.247</td>
<td>4.450</td>
</tr>
<tr>
<td>8</td>
<td>0.235</td>
<td>35.96</td>
<td>37,893</td>
<td>2.122</td>
<td>3.401</td>
<td>2.940</td>
</tr>
<tr>
<td>9</td>
<td>0.241</td>
<td>32.94</td>
<td>40,421</td>
<td>2.262</td>
<td>3.625</td>
<td>2.759</td>
</tr>
<tr>
<td>10</td>
<td>0.362</td>
<td>21.54</td>
<td>62,464</td>
<td>3.496</td>
<td>5.603</td>
<td>1.785</td>
</tr>
<tr>
<td>11</td>
<td>0.469</td>
<td>16.25</td>
<td>69,023</td>
<td>3.864</td>
<td>6.192</td>
<td>1.615</td>
</tr>
<tr>
<td>12</td>
<td>0.701</td>
<td>9.08</td>
<td>96,744</td>
<td>5.416</td>
<td>8.679</td>
<td>1.152</td>
</tr>
<tr>
<td>13</td>
<td>0.121</td>
<td>67.09</td>
<td>18,422</td>
<td>1.032</td>
<td>0.827</td>
<td>12.092</td>
</tr>
<tr>
<td>14</td>
<td>0.235</td>
<td>35.96</td>
<td>30,542</td>
<td>1.710</td>
<td>1.370</td>
<td>7.299</td>
</tr>
<tr>
<td>15</td>
<td>0.241</td>
<td>32.94</td>
<td>36,222</td>
<td>2.028</td>
<td>1.625</td>
<td>6.154</td>
</tr>
<tr>
<td>16</td>
<td>0.362</td>
<td>21.54</td>
<td>50,123</td>
<td>2.806</td>
<td>2.248</td>
<td>4.448</td>
</tr>
<tr>
<td>17</td>
<td>0.469</td>
<td>16.25</td>
<td>63,545</td>
<td>3.558</td>
<td>2.851</td>
<td>3.507</td>
</tr>
<tr>
<td>18</td>
<td>0.483</td>
<td>15.84</td>
<td>63,405</td>
<td>3.550</td>
<td>2.845</td>
<td>3.515</td>
</tr>
<tr>
<td>19</td>
<td>1.211</td>
<td>5.45</td>
<td>121,670</td>
<td>6.810</td>
<td>5.457</td>
<td>1.833</td>
</tr>
</tbody>
</table>

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Table 21. (Continued)

<table>
<thead>
<tr>
<th>Run</th>
<th>[RSH]</th>
<th>[M]/[RSH]</th>
<th>dpm</th>
<th>Moles ØH x 10^6</th>
<th>Rf x 10^7c x 10^-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.422</td>
<td>2.05</td>
<td>189,052</td>
<td>10.582</td>
<td>8.479</td>
</tr>
<tr>
<td>21</td>
<td>3.633</td>
<td>0.91</td>
<td>239,584</td>
<td>13.410</td>
<td>10.745</td>
</tr>
<tr>
<td>22</td>
<td>6.054</td>
<td>0.00</td>
<td>212,954</td>
<td>11.920</td>
<td>9.551</td>
</tr>
</tbody>
</table>

a) Molarity of PAT is 416 x 10^-3 for runs 1-6, 13-20, and 8.32 x 10^-3 for runs 7-12.

b) Specific activity of the thiol is 4.845 x 10^{10} dpm/mole for runs 1-6 and 3.573 x 10^{10} dpm/mole for runs 7-22.

c) The time is 1.2 x 10^3 sec for runs 1-12 and 2.4 x 10^3 sec for runs 13-22.
Figure 15. The Relative Rate of Addition of the Phenyl Radical to Styrene, \([I]_0 = 4.16 \times 10^{-3}\), \(t = 2.4 \times 10^3\) sec.
Table 22. The Relative Rate of Addition of the Phenyl Radical to \( \alpha \)-Methylstyrene

<table>
<thead>
<tr>
<th>Run^a</th>
<th>[RSH]</th>
<th>[N]/[RSH]</th>
<th>dpm^b</th>
<th>Moles OH x 10^6</th>
<th>R_f x 10^7c</th>
<th>1/R_f x 10^-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.125</td>
<td>57.34</td>
<td>11,266</td>
<td>0.630</td>
<td>1.010</td>
<td>9.901</td>
</tr>
<tr>
<td>2</td>
<td>0.242</td>
<td>28.95</td>
<td>22,138</td>
<td>1.240</td>
<td>1.987</td>
<td>5.033</td>
</tr>
<tr>
<td>3</td>
<td>0.250</td>
<td>28.12</td>
<td>22,260</td>
<td>1.246</td>
<td>1.997</td>
<td>5.088</td>
</tr>
<tr>
<td>4</td>
<td>0.374</td>
<td>18.37</td>
<td>31,624</td>
<td>1.770</td>
<td>2.837</td>
<td>3.525</td>
</tr>
<tr>
<td>5</td>
<td>0.499</td>
<td>13.50</td>
<td>43,590</td>
<td>2.440</td>
<td>3.910</td>
<td>2.558</td>
</tr>
<tr>
<td>6</td>
<td>0.727</td>
<td>8.88</td>
<td>62,054</td>
<td>3.474</td>
<td>5.567</td>
<td>1.796</td>
</tr>
<tr>
<td>7</td>
<td>0.125</td>
<td>57.34</td>
<td>17,684</td>
<td>0.990</td>
<td>0.793</td>
<td>12.610</td>
</tr>
<tr>
<td>8</td>
<td>0.242</td>
<td>28.95</td>
<td>31,968</td>
<td>1.790</td>
<td>1.434</td>
<td>6.974</td>
</tr>
<tr>
<td>9</td>
<td>0.250</td>
<td>28.12</td>
<td>35,090</td>
<td>1.964</td>
<td>1.574</td>
<td>6.353</td>
</tr>
<tr>
<td>10</td>
<td>0.374</td>
<td>18.37</td>
<td>50,016</td>
<td>2.800</td>
<td>2.244</td>
<td>4.456</td>
</tr>
<tr>
<td>11</td>
<td>0.499</td>
<td>13.50</td>
<td>67,735</td>
<td>3.792</td>
<td>3.038</td>
<td>3.292</td>
</tr>
<tr>
<td>12</td>
<td>0.727</td>
<td>8.88</td>
<td>86,784</td>
<td>4.858</td>
<td>3.893</td>
<td>2.569</td>
</tr>
</tbody>
</table>

a) Molarity of PAT is \( 4.16 \times 10^{-3} \).

b) Specific activity of the thiol is \( 3.573 \times 10^{10} \) dpm/mole.

c) The time is \( 1.2 \times 10^3 \) sec for runs 1-6 and \( 2.4 \times 10^3 \) sec for runs 7-12.
Figure 16. The Relative Rate of Addition of the Phenyl Radical to γ-Methylstyrene, \( t = 2.4 \times 10^3 \) sec.

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Figure 17. The Relative Rate of Addition of the Phenyl Radical to Styrene, \([I]_0 = 8.32 \times 10^{-3}\), \(t = 1.2 \times 10^3\) sec.

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Figure 18. The Relative Rate of Addition of the Phenyl Radical to Styrene, $[I]_0 = 4.16 \times 10^{-3}$, $t = 1.2 \times 10^3$ sec.
Figure 19. The Relative Rate of Addition of the Phenyl Radical to α-Methylstyrene, $t = 1.2 \times 10^3$ sec.
**Table 23. The Relative Rate of Addition of the Phenyl Radical to 2-Vinyl Pyridine**

<table>
<thead>
<tr>
<th>Run</th>
<th>[RSH]</th>
<th>[M]/[RSH]</th>
<th>dpm $^b$</th>
<th>Moles $\delta$H $^{x10^6}$</th>
<th>$R_F^{x10^7}$ $^{c}$</th>
<th>$1/R_F$ $^{x10^{-6}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.282</td>
<td>28.01</td>
<td>18,603</td>
<td>0.768</td>
<td>1.231</td>
<td>8.123</td>
</tr>
<tr>
<td>2</td>
<td>0.356</td>
<td>23.43</td>
<td>20,611</td>
<td>0.850</td>
<td>1.362</td>
<td>7.342</td>
</tr>
<tr>
<td>3</td>
<td>0.475</td>
<td>17.23</td>
<td>29,365</td>
<td>1.212</td>
<td>1.942</td>
<td>5.149</td>
</tr>
<tr>
<td>4</td>
<td>0.725</td>
<td>10.77</td>
<td>46,381</td>
<td>1.914</td>
<td>3.067</td>
<td>3.261</td>
</tr>
</tbody>
</table>

a) Molarity of PAT is $4.16 \times 10^{-3}$.

b) Specific activity of the thiol is $4.845 \times 10^{10}$ dpm/mole.

c) The time is $1.2 \times 10^3$ sec.
Figure 20. The Relative Rate of Addition of the Phenyl Radical to 2-Vinyl Pyridine

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Table 24. The Relative Rate of Addition of the Phenyl Radical to Allyl Acetate

<table>
<thead>
<tr>
<th>Run&lt;sup&gt;a&lt;/sup&gt;</th>
<th>[RSH]</th>
<th>[M]/[RSH]</th>
<th>dpm&lt;sup&gt;b&lt;/sup&gt; x 10&lt;sup&gt;5&lt;/sup&gt;</th>
<th>Moles OH&lt;sup&gt;c&lt;/sup&gt;</th>
<th>R&lt;sub&gt;f&lt;/sub&gt; x 10&lt;sup&gt;7&lt;/sup&gt; x 10&lt;sup&gt;-6&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.108</td>
<td>79.88</td>
<td>22,358</td>
<td>1.188</td>
<td>1.904</td>
</tr>
<tr>
<td>2</td>
<td>0.147</td>
<td>58.16</td>
<td>30,526</td>
<td>1.623</td>
<td>2.601</td>
</tr>
<tr>
<td>3</td>
<td>0.216</td>
<td>39.26</td>
<td>42,119</td>
<td>2.239</td>
<td>3.588</td>
</tr>
<tr>
<td>4</td>
<td>0.323</td>
<td>30.58</td>
<td>54,253</td>
<td>2.911</td>
<td>4.665</td>
</tr>
<tr>
<td>5</td>
<td>0.432</td>
<td>18.95</td>
<td>79,040</td>
<td>4.202</td>
<td>6.734</td>
</tr>
</tbody>
</table>

a) Molarity of PAT is 4.16 x 10<sup>-3</sup>.
b) Specific activity of the thiol is 3.762 x 10<sup>10</sup> dpm/mole.
c) The time is 1.2 x 10<sup>3</sup> sec.
Figure 21. The Relative Rate of Addition of the Phenyl Radical to Allyl Acetate
Table 25. The Relative Rate of Addition of the Phenyl Radical to Vinyl Acetate

<table>
<thead>
<tr>
<th>Run(^a)</th>
<th>[RSH]</th>
<th>[M]/[RSH]</th>
<th>dpm(^b)</th>
<th>Moles (\Phi H) x10(^6)</th>
<th>(1/R_F) x10(^7)</th>
<th>(1/R_F) x10(^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.117</td>
<td>86.02</td>
<td>38,458</td>
<td>2.044</td>
<td>3.276</td>
<td>3.052</td>
</tr>
<tr>
<td>2</td>
<td>0.190</td>
<td>52.49</td>
<td>56,577</td>
<td>3.008</td>
<td>4.936</td>
<td>2.026</td>
</tr>
<tr>
<td>3</td>
<td>0.233</td>
<td>42.19</td>
<td>67.172</td>
<td>3.572</td>
<td>5.724</td>
<td>1.747</td>
</tr>
<tr>
<td>4</td>
<td>0.352</td>
<td>33.85</td>
<td>78,776</td>
<td>4.188</td>
<td>6.712</td>
<td>1.490</td>
</tr>
<tr>
<td>5</td>
<td>0.466</td>
<td>20.28</td>
<td>119,278</td>
<td>6.342</td>
<td>10.163</td>
<td>0.984</td>
</tr>
</tbody>
</table>

\(^a\) Molarity of PAT is 4.16 x 10\(^{-3}\).  
\(^b\) Specific activity of the thiol is 3.762 x 10\(^{10}\) dpm/mole.  
\(^c\) The time is 1.2 x 10\(^3\) sec.
Figure 22. The Relative Rate of Addition of the Phenyl Radical of Vinyl Acetate.
Table 26. The Relative Rate of Addition of the Phenyl Radical to Diethyl Maleate

<table>
<thead>
<tr>
<th>Run</th>
<th>[RSH]</th>
<th>[M]/[RSH]</th>
<th>dpm $\times 10^6$</th>
<th>Moles $\cdot H$ $\times 10^6$</th>
<th>$R_f \times 10^7$ $\times 10^{-6}$</th>
<th>$1/R_f$ $\times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.118</td>
<td>48.93</td>
<td>20,530</td>
<td>1.092</td>
<td>1.750</td>
<td>5.714</td>
</tr>
<tr>
<td>2</td>
<td>0.146</td>
<td>39.31</td>
<td>24,749</td>
<td>1.316</td>
<td>2.109</td>
<td>4.742</td>
</tr>
<tr>
<td>3</td>
<td>0.236</td>
<td>24.05</td>
<td>37,280</td>
<td>1.982</td>
<td>3.176</td>
<td>3.149</td>
</tr>
<tr>
<td>4</td>
<td>0.291</td>
<td>19.21</td>
<td>46,699</td>
<td>2.482</td>
<td>3.978</td>
<td>2.514</td>
</tr>
<tr>
<td>5</td>
<td>0.582</td>
<td>9.17</td>
<td>78,673</td>
<td>4.182</td>
<td>6.702</td>
<td>1.492</td>
</tr>
</tbody>
</table>

a) Molarity of PAT is $4.16 \times 10^{-3}$.

b) Specific Activity of the thiol is $3.762 \times 10^{10}$ dpm/mole.

c) The time is $1.2 \times 10^3$ sec.
Figure 23. The Relative Rate of Addition of the Phenyl Radical to Diethyl Maleate
Table 27. The Relative Rate of Addition of the Phenyl Radical to Methyl Acrylate

<table>
<thead>
<tr>
<th>Run</th>
<th>[RSH]</th>
<th>[M]/[RSH]</th>
<th>dpm$^b$</th>
<th>Moles $\phi_H$x10$^6$</th>
<th>R$_f$x10$^7$c</th>
<th>1/R$_f$x10$^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.174</td>
<td>59.10</td>
<td>24,332</td>
<td>0.948</td>
<td>1.519</td>
<td>6.583</td>
</tr>
<tr>
<td>2</td>
<td>0.347</td>
<td>28.71</td>
<td>49,798</td>
<td>1.938</td>
<td>3.106</td>
<td>3.220</td>
</tr>
<tr>
<td>3</td>
<td>0.480</td>
<td>20.27</td>
<td>66,730</td>
<td>2.598</td>
<td>4.163</td>
<td>2.402</td>
</tr>
<tr>
<td>4</td>
<td>0.694</td>
<td>13.51</td>
<td>89,716</td>
<td>3.492</td>
<td>5.596</td>
<td>1.787</td>
</tr>
<tr>
<td>5</td>
<td>1.210</td>
<td>6.97</td>
<td>144,944</td>
<td>5.642</td>
<td>9.042</td>
<td>1.106</td>
</tr>
<tr>
<td>6</td>
<td>1.439</td>
<td>5.61</td>
<td>164,157</td>
<td>6.390</td>
<td>10.240</td>
<td>0.977</td>
</tr>
</tbody>
</table>

a) Molarity of PAT is 4.16 x 10$^{-3}$.

b) Specific activity of the thiol is 5.139 x 10$^{10}$ dpm/mole.

c) The time is 1.2 x 10$^3$ sec.
Figure 24. The Relative Rate of Addition of the Phenyl Radical to Methyl Acrylate
Table 28. The Relative Rate of Addition of the Phenyl Radical to Methyl Methacrylate

<table>
<thead>
<tr>
<th>Run^a</th>
<th>[RSH]</th>
<th>[M]/[RSH]</th>
<th>dpm^b</th>
<th>Moles φH x10^6</th>
<th>Rf x10^7c</th>
<th>1/Rf x10^-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.178</td>
<td>48.98</td>
<td>13,541</td>
<td>0.526</td>
<td>0.843</td>
<td>11.862</td>
</tr>
<tr>
<td>2</td>
<td>0.356</td>
<td>23.77</td>
<td>27,116</td>
<td>1.056</td>
<td>1.692</td>
<td>5.910</td>
</tr>
<tr>
<td>3</td>
<td>0.391</td>
<td>21.49</td>
<td>30,520</td>
<td>1.190</td>
<td>1.907</td>
<td>5.244</td>
</tr>
<tr>
<td>4</td>
<td>0.711</td>
<td>11.15</td>
<td>61,783</td>
<td>2.404</td>
<td>3.853</td>
<td>2.595</td>
</tr>
<tr>
<td>5</td>
<td>1.173</td>
<td>6.19</td>
<td>91,649</td>
<td>3.568</td>
<td>5.718</td>
<td>1.749</td>
</tr>
</tbody>
</table>

a) The molarity of PAT is 4.16 x 10^-3.

b) Specific activity of the thiol is 5.139 x 10^{10} dpm/mole.

c) The time is 1.2 x 10^3 sec.
Figure 25. The Relative Rate of Addition of the Phenyl Radical to Methyl Methacrylate
Table 29.  The Relative Rate of Addition of the Phenyl Radical to Methacrylonitrile

<table>
<thead>
<tr>
<th>Run</th>
<th>[RSH]</th>
<th>[M]/[RSH]</th>
<th>dpm</th>
<th>Moles $\Phi_H$ x10^6</th>
<th>$R_f$ x10^7c</th>
<th>1/R_f x10^6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.258</td>
<td>42.14</td>
<td>10,823</td>
<td>0.446</td>
<td>0.715</td>
<td>13.986</td>
</tr>
<tr>
<td>2</td>
<td>0.366</td>
<td>29.11</td>
<td>16,724</td>
<td>0.690</td>
<td>1.106</td>
<td>9.842</td>
</tr>
<tr>
<td>3</td>
<td>0.516</td>
<td>20.18</td>
<td>22,972</td>
<td>0.948</td>
<td>1.519</td>
<td>6.583</td>
</tr>
<tr>
<td>4</td>
<td>0.732</td>
<td>13.64</td>
<td>32,905</td>
<td>1.358</td>
<td>2.176</td>
<td>4.596</td>
</tr>
<tr>
<td>5</td>
<td>1.093</td>
<td>9.19</td>
<td>48,321</td>
<td>1.994</td>
<td>3.196</td>
<td>3.129</td>
</tr>
</tbody>
</table>

a) Molarity of PAT is 4.16 x 10^{-3}.
b) Specific activity of the thiol is 4.845 x 10^{10} dpm/mole.
c) The time is 1.2 x 10^{3} sec.
Figure 26. The Relative Rate of Addition of the Phenyl Radical to Methacrylonitrile

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Table 30. Summary of the Relative Rates of Addition of Phenyl Radicals to Polymerizable Olefins

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$\frac{k_i}{k_H k_d f[I]} \times 10^{-4}$</th>
<th>$\frac{1}{k_d f[I]} \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>$13.46 \pm 0.01$</td>
<td>$0.66 \pm 0.02$</td>
</tr>
<tr>
<td>α-Methylstyrene</td>
<td>$16.64 \pm 0.03$</td>
<td>$0.33 \pm 0.02$</td>
</tr>
<tr>
<td>Vinyl Acetate</td>
<td>$3.10 \pm 0.01$</td>
<td>$0.41 \pm 0.01$</td>
</tr>
<tr>
<td>Allyl Acetate</td>
<td>$6.17 \pm 0.01$</td>
<td>$0.30 \pm 0.01$</td>
</tr>
<tr>
<td>Diethyl Maleate</td>
<td>$10.68 \pm 0.01$</td>
<td>$0.52 \pm 0.02$</td>
</tr>
<tr>
<td>Methacrylonitrile</td>
<td>$33.15 \pm 0.11$</td>
<td>$0.05 \pm 0.01$</td>
</tr>
<tr>
<td>2-Vinyl Pyridine</td>
<td>$29.18 \pm 0.44$</td>
<td>$0.17 \pm 0.05$</td>
</tr>
<tr>
<td>Methyl Methacrylate</td>
<td>$23.98 \pm 0.07$</td>
<td>$0.12 \pm 0.01$</td>
</tr>
<tr>
<td>Methyl Acrylate</td>
<td>$10.45 \pm 0.01$</td>
<td>$0.34 \pm 0.01$</td>
</tr>
</tbody>
</table>

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Table 31. The Relative Reactivity of the Methyl and Polystyryl Radicals with Various Monomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$k_{11}/k_1$ for Methyl Radical$^b$</th>
<th>$\log(k_{11}/k_1)$</th>
<th>Ref.</th>
<th>$r_1$ for Styrene$^c$</th>
<th>$\log(100/r_1)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>792</td>
<td>2.899</td>
<td>24</td>
<td>0.000</td>
<td>2.000</td>
<td></td>
</tr>
<tr>
<td>α-Methylstyrne</td>
<td>926</td>
<td>2.967</td>
<td>24</td>
<td>2.180$^a$</td>
<td>0.260</td>
<td>76</td>
</tr>
<tr>
<td>Vinyl Acetate</td>
<td>37</td>
<td>1.568</td>
<td>23</td>
<td>55.000</td>
<td>0.885</td>
<td>77</td>
</tr>
<tr>
<td>Diethyl Maleate</td>
<td>264</td>
<td>2.121</td>
<td>23</td>
<td>6.52</td>
<td>2.250</td>
<td>77</td>
</tr>
<tr>
<td>2-Vinyl Pyridine</td>
<td>1,360</td>
<td>3.134</td>
<td>73</td>
<td>0.54</td>
<td>2.250</td>
<td>78</td>
</tr>
<tr>
<td>4-Vinyl Pyridine</td>
<td>1,360</td>
<td>3.134</td>
<td>73</td>
<td>0.54</td>
<td>2.250</td>
<td>78</td>
</tr>
<tr>
<td>Methyl Acrylate</td>
<td>1,030</td>
<td>3.013</td>
<td>74</td>
<td>0.75</td>
<td>2.125</td>
<td>79</td>
</tr>
<tr>
<td>Maleonitrile</td>
<td>2.976$^a$</td>
<td>0.19</td>
<td>2.420</td>
<td>85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fumaronitrile</td>
<td>2.976$^a$</td>
<td>0.19</td>
<td>2.420</td>
<td>85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethyl Fumarate</td>
<td>2.987$^a$</td>
<td>0.301</td>
<td>2.220</td>
<td>79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butadiene-1,3</td>
<td>2,015</td>
<td>3.003</td>
<td>75</td>
<td>1.78</td>
<td>1.807</td>
<td>77</td>
</tr>
<tr>
<td>2,3-Dimethylbutadiene</td>
<td>2,230</td>
<td>3.047</td>
<td>75</td>
<td>1.725$^a$</td>
<td>1.725$^a$</td>
<td>83</td>
</tr>
<tr>
<td>Isoprene</td>
<td>2,090</td>
<td>3.019</td>
<td>75</td>
<td>1.38</td>
<td>1.559</td>
<td>83</td>
</tr>
</tbody>
</table>
Table 31 (continued)

<table>
<thead>
<tr>
<th>Material</th>
<th>ν</th>
<th>ω</th>
<th>β</th>
<th>r₁</th>
<th>ϰ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Methacrylate</td>
<td>1,440</td>
<td>3.158</td>
<td>74</td>
<td>0.50</td>
<td>2.301</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>1,730</td>
<td>3.238</td>
<td>74</td>
<td>0.50</td>
<td>2.301</td>
</tr>
<tr>
<td>Methacrylonitrile</td>
<td>2,120</td>
<td>3.326</td>
<td>74</td>
<td>0.30</td>
<td>2.523</td>
</tr>
<tr>
<td>Allyl Acetate</td>
<td></td>
<td>1.750&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>90.00</td>
<td>0.046</td>
</tr>
<tr>
<td>Chloroprene</td>
<td>7,540</td>
<td>3.576</td>
<td>75</td>
<td>0.052</td>
<td>2.983</td>
</tr>
<tr>
<td>Methyl Vinyl Ketone</td>
<td>1,900</td>
<td>3.279</td>
<td>74</td>
<td>0.29</td>
<td>2.538</td>
</tr>
<tr>
<td>Maleic Anhydride</td>
<td></td>
<td>3.278&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>0.02</td>
<td>3.398</td>
</tr>
</tbody>
</table>

a) Interpolated from Figure 6, p. 28 of Reference 6.

b) Data of Szwarc. See discussion on p. 17 and references cited in fourth column.

c) r₁ is the reactivity ratio in copolymerizations. See discussion on p. 96 and references in last column.
Figure 27. The Relative Rates of Addition of the Polystyryl and Methyl Radicals to Monomers. Data from Table 31.

Slope = 1.25

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Figure 28. The Relative Rates of Additions of the Polystyryl and Phenyl Radicals to Monomers. Data from Tables 30 and 31.
Figure 29. The Relative Rates of Additions of the Methyl and Phenyl Radicals to Monomers. Data from Tables 30 and 31.
Table 32. The Relative Rate of Hydrogen Abstraction from Toluene, Ethylbenzene and Cumene for the Phenyl, Methyl, and Polystyryl Radicals

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Phenyl (1.00^a)</th>
<th>Methyl (1.00^b)</th>
<th>Polystyryl (1.00^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>(3.23^{34})</td>
<td>(4.03^{86})</td>
<td>(8.29^{c})</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>(7.15^{34})</td>
<td>(13.00^{86})</td>
<td>(19.61^{d})</td>
</tr>
<tr>
<td>Cumene</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Based on toluene = 1.00.
b) An average value of the data in References, 87, 88, 89, and 90.
c) An average value of the data in References 91 and 92.
d) An average value of the data in References 90 and 92.
Table 33. The Relative Rate of Addition of the Poly (Methyl Methacrylate) Radical to Polymerizable Olefins.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$r_1$</th>
<th>$1/r_1$</th>
<th>$\log(100/nr_1)$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile</td>
<td>1.20</td>
<td>0.833</td>
<td>1.921</td>
<td>80</td>
</tr>
<tr>
<td>Allyl Acetate</td>
<td>23.00</td>
<td>0.043</td>
<td>0.633</td>
<td>82</td>
</tr>
<tr>
<td>Maleic Anhydride</td>
<td>3.50</td>
<td>0.286</td>
<td>1.155</td>
<td>97</td>
</tr>
<tr>
<td>Methacrylonitrile</td>
<td>0.67</td>
<td>1.493</td>
<td>2.174</td>
<td>77</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.50</td>
<td>2.000</td>
<td>2.301</td>
<td>80</td>
</tr>
<tr>
<td>Vinyl Acetate</td>
<td>20.00</td>
<td>0.050</td>
<td>0.699</td>
<td>76</td>
</tr>
<tr>
<td>2-Vinyl Pyridine</td>
<td>0.44</td>
<td>2.272</td>
<td>2.356</td>
<td>78</td>
</tr>
<tr>
<td>4-Vinyl Pyridine</td>
<td>0.57</td>
<td>1.754</td>
<td>2.244</td>
<td>78</td>
</tr>
<tr>
<td>Diethyl Maleate</td>
<td>20.00</td>
<td>0.050</td>
<td>0.398</td>
<td>82</td>
</tr>
<tr>
<td>$\alpha$-Methylstylene</td>
<td>0.50</td>
<td>2.000</td>
<td>2.301</td>
<td>98</td>
</tr>
</tbody>
</table>
Figure 30. The Relative Rates of Additions of the Polystyryl and Poly(methyl methacrylate) Radicals to Monomers.
Table 34. The Relative Rates of Addition of Methyl and Benzoyloxy Radicals to Phenyl Substituted Ethylenes

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$k_{ij}/k_i$ for Methyl Radical</th>
<th>$\log(k_{ij}/nk_i)$</th>
<th>Ref.</th>
<th>$k_{ij}/k_i$ for Phenyl Radical</th>
<th>$\log(k_{ij}/k_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>792</td>
<td>2.899</td>
<td>24</td>
<td>2.6</td>
<td>0.415</td>
</tr>
<tr>
<td>trans-Stilbene</td>
<td>104</td>
<td>2.017</td>
<td>24</td>
<td>12.4</td>
<td>0.792</td>
</tr>
<tr>
<td>cis-Stilbene</td>
<td>29</td>
<td>1.462</td>
<td>6</td>
<td>8.3</td>
<td>0.618</td>
</tr>
<tr>
<td>1,1-Diphenylethylene</td>
<td>1,590</td>
<td>3.201</td>
<td>6</td>
<td>7.7</td>
<td>0.886</td>
</tr>
<tr>
<td>Triphenylethylene</td>
<td>46</td>
<td>1,663</td>
<td>6</td>
<td>11.7</td>
<td>1.086</td>
</tr>
</tbody>
</table>
Figure 31. The Relative Rates of Additions of the Methyl and Benzoyloxy Radicals to Monomers.
REFERENCES


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VITA

Thomas Raymond Fiske was born in Salem, Oregon on June 22, 1940. He was educated in the Salem Public School System, graduating from North Salem High School in June of 1958. He entered Willamette University in September of 1958 and received the Bachelor of Arts degree in June of 1962. He then entered Purdue University in September of 1962 and received the Master of Science degree in Chemistry in January of 1965.

He entered the graduate school of Louisiana State University in September of 1964, and was awarded a research assistantship from the Dow Chemical Company, Louisiana Division.

He was married to the former Sally Ann Shurr, in Frankfort, Indiana, in June of 1964. He obtained a legal separation in September of 1967.

He is currently a candidate for the degree of Doctor of Philosophy at Louisiana State University, Baton Rouge, Louisiana.
Candidate: Thomas Raymond Fiske

Major Field: Chemistry

Title of Thesis: Problems in Radical Polymerizations I. The Isotope Effect on Hydrogen Abstraction from Chloroform by the Polystyryl Radical II. The Transfer Constant of AlBN III. A Scale of Phenyl Affinities.

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

EXAMINATION AND THESIS REPORT

Date of Examination: October 26, 1967

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