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Inhibitors and Retarders for the Free Radical Polymerization of Alpha-Methylstyrene

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INHIBITORS AND RETARDERS FOR THE FREE RADICAL POLYMERIZATION OF ALPHA-METHYLSTYRENE

by

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I. INTRODUCTION

The intent of this work was to determine the effect of a variety of compounds on the peroxide-initiated free radical polymerization of ∝-methylstyrene. All of the compounds tested are known to act as inhibitors or retarders in the free radical polymerization of other monomers, but their effect on the polymerization of ∝-methylstyrene had not yet been determined.

The term inhibitor is used here to describe a compound that will completely suppress polymerization, producing an induction period. Figure 1 is a % polymerization versus time plot for the free radical polymerization of styrene initiated with azo-isobutyronitrile and inhibited by p-benzoquinone.[1] It can be seen from Figure 1 that p-benzoquinone is not an ideal inhibitor for the polymerization of styrene. After a short induction period, there is a slow polymerization which changes abruptly to a fast reaction with all the characteristics of a normal polymerization.

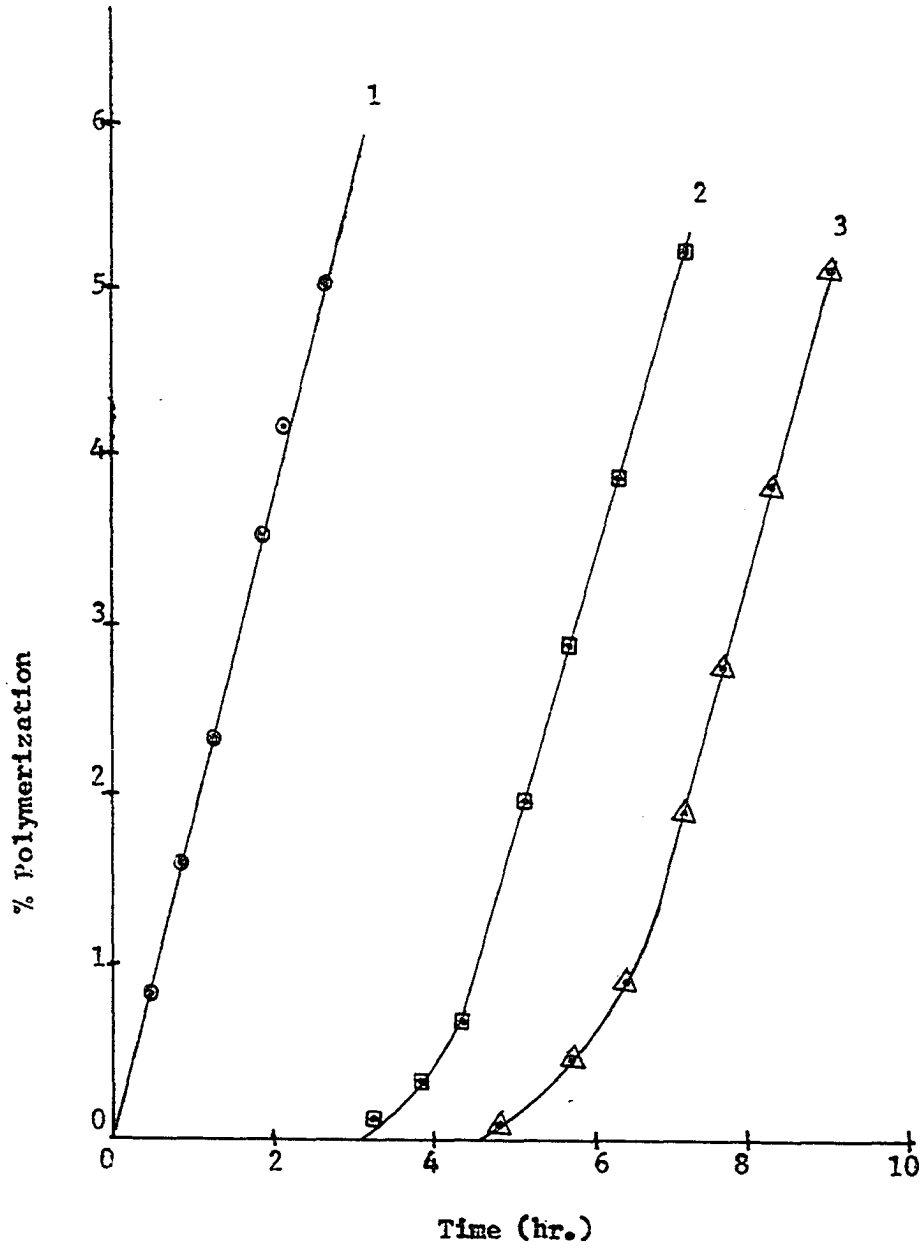


Figure 1: Conversion-time plots for experiments involving styrene, azo-isobutyronitrile and benzoquinone. The numbers correspond to benzoquinone concentrations of: (1) 0; (2) 0.075; (3) 0.123 g/l. Initiator concentration 0.5 g/l.

Retarders are less efficient than inhibitors and only slow, rather than stop, the polymerization process. Figure 2 shows the retarding effect of nitrobenzene on the polymerization of vinyl acetate initiated with benzoyl peroxide.[2]

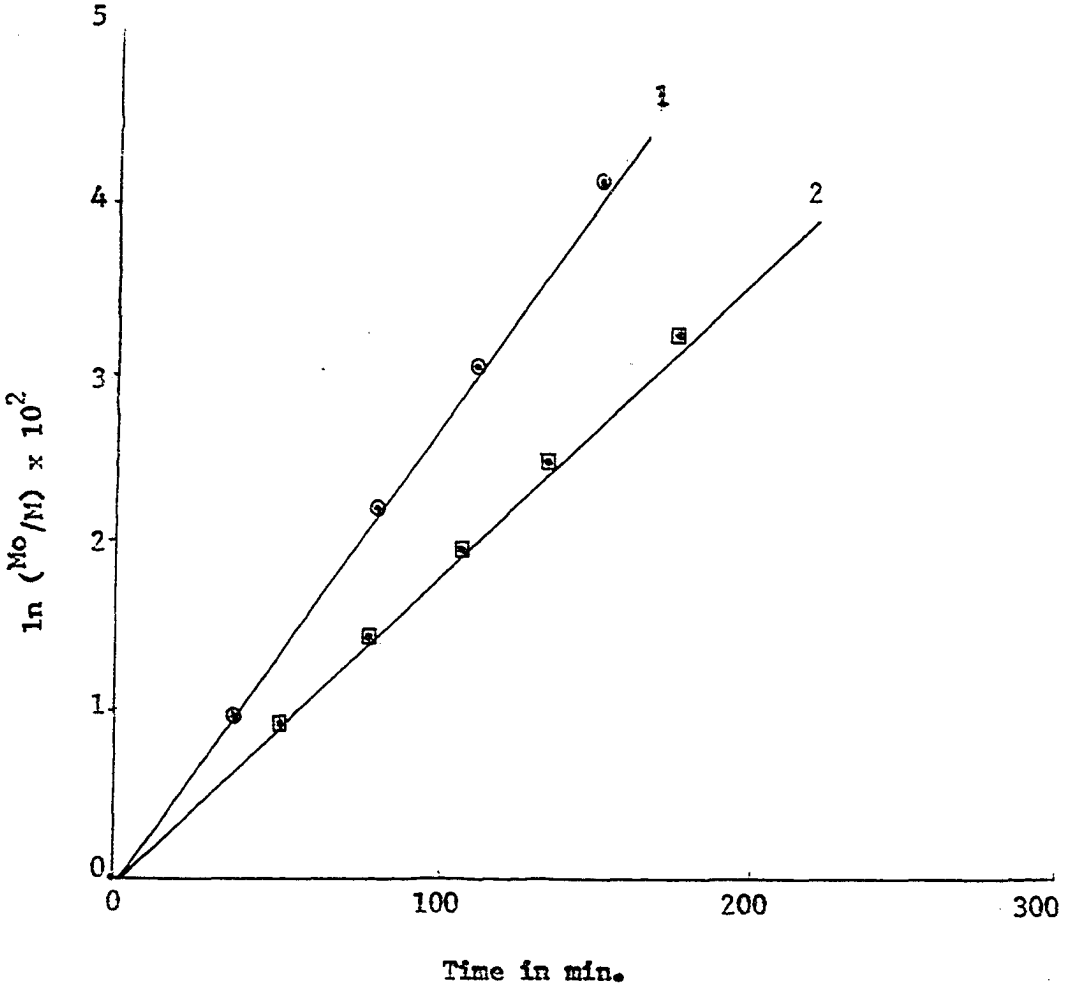


Figure 2: Conversion-time plots for experiments involving vinyl acetate, benzoyl peroxide, and nitrobenzene. The numbers correspond to nitrobenzene concentrations of: (1) 0; (2) 4.5×10^{-3}M. Initiator concentration of 1.7×10^{-2}M.

Classifying compounds as inhibitors or retarders is an attempt to distinguish them according to their effectiveness as chain terminators. Their classification, however, does not necessarily imply a difference in reaction mechanism.

The effect of a known chain terminator on free radical polymerization is dependent not only on the nature of the terminator, but also upon that of the monomer. As can be seen from Figure 1, for the polymerization of styrene benzoquinone is an inhibitor; in methyl methacrylate, however, benzoquinone is a retarder.[3] (Figure 3)

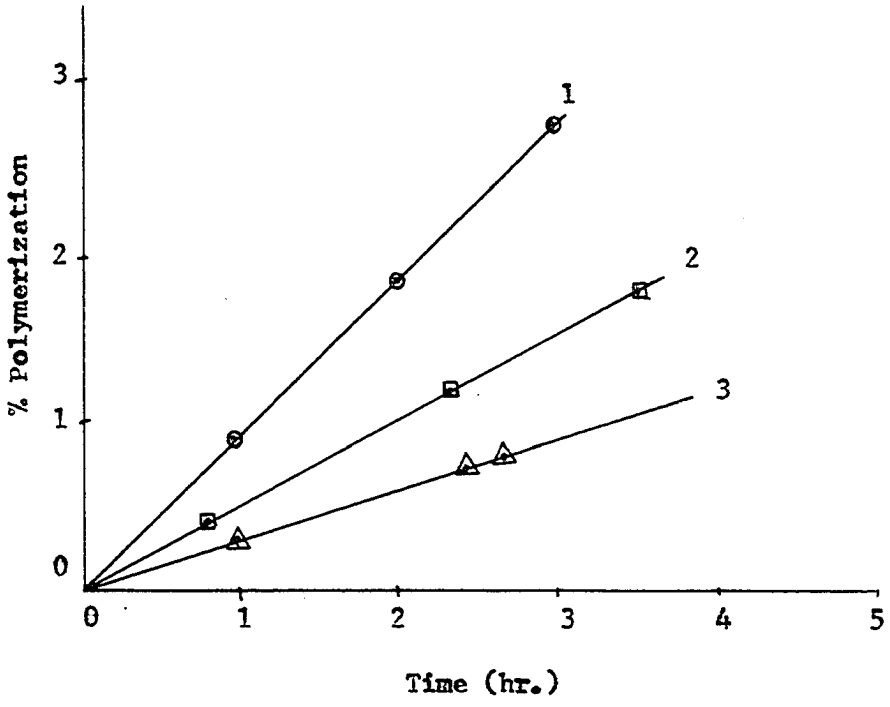


Figure 3: Conversion-time plots for experiments involving methyl methacrylate, azo-isobutyronitrile and benzoquinone. The numbers correspond to benzoquinone concentrations of (1) 0; (2) 0.2: (3) 0.352. Initiator concentration of 0.5 g/l.

In this work, two general types of terminators were used:

A. Nonradical Terminators

These are compounds that are not themselves radicals, but can react with free radicals to form more stable compounds that do not continue the polymerization process.

B. A Stable Free Radical

2,2-Diphenyl-1-picrylhydrazyl (DPPH) because of its stability does not initiate polymerization, but it can scavenge other radicals in the system.

A. Nonradical Terminators

A nonradical terminator is a substance that reacts with radicals in a manner to produce another radical that is too stable to continue the polymerization process. Quinones and nitro compounds have long been known to be effective nonradical terminators for various polymerization systems. The specific effect of these terminators, however, is very dependent on the nature of the monomer.

Benzoquinone and duroquinone give sharp induction periods in the benzoyl peroxide initiated polymerization of vinyl acetate, after which the reaction proceeds at an uninhibited rate. The length of the induction period, in both cases, corresponds to a stoichiometry in which one quinone molecule stops one kinetic chain.

The effects of benzoquinone upon the sensitized polymerizations of styrene[1] and methyl methacrylate[3] have been studied using ^{14}C azo-isobutyronitrile as a sensitizer.

In the polymerization of methyl methacrylate, Fig. 3, benzo-

quinone is shown to be a retarder and the degree of retardation is directly proportional to the concentration of benzoquinone. By using labeled initiator, Bevington et al.,[3] were able to show that the growing polymer radicals react with benzoquinone to give fairly unreactive radicals, most of which terminate by combination reactions with ordinary polymer radicals. In the following mechanism R• is any radical capable of propagation, Q is benzoquinone, M is monomer, I is initiator, and P is a polymer chain.

Initiation	$I \longrightarrow 2R\bullet$
Propagation	$R\bullet + M \longrightarrow R\bullet$
	$R\bullet + Q \longrightarrow PQ\bullet$
Termination	$PQ\bullet + R\bullet \longrightarrow PQR$

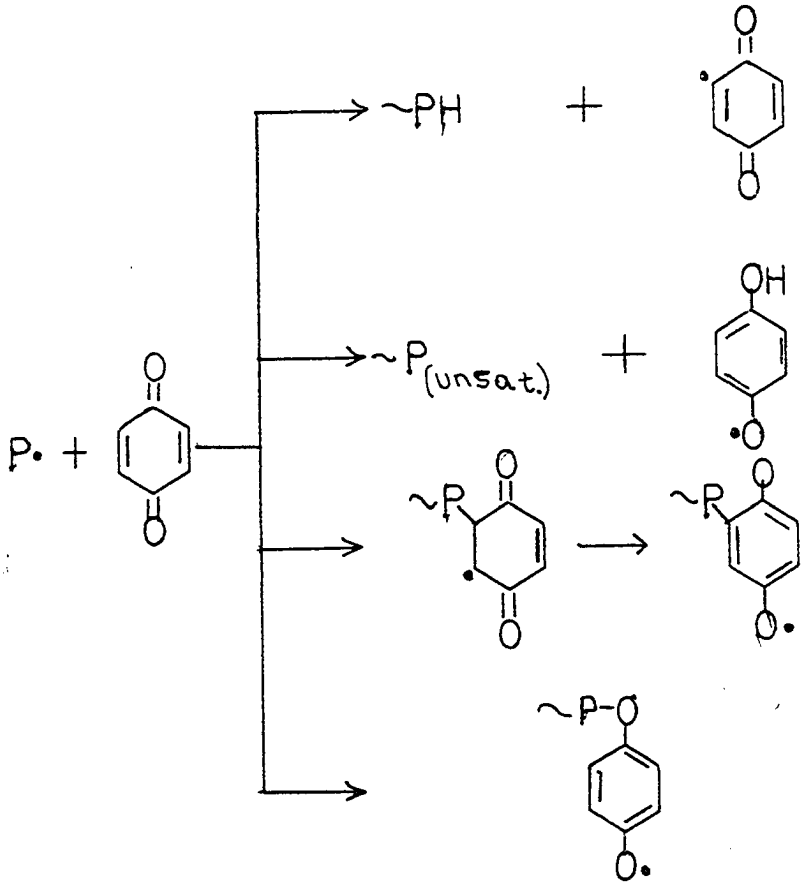
When labeled initiator and inhibitor were used in the polymerization of styrene, the slow polymerization (Fig. 1) was shown to produce a polymer of low molecular weight with combined benzoquinone. There is, therefore, a copolymerization of styrene with benzoquinone during the slow process.

$$R\bullet + Q \longrightarrow PQ\bullet$$

$$PQ\bullet + M \longrightarrow PQR\bullet$$

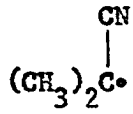
When all of the benzoquinone is consumed, the rate of polymerization rises to its normal uninhibited value.

Mechanisms by which p-benzoquinone might react with polymer radicals have been summarized by Walling.[4]

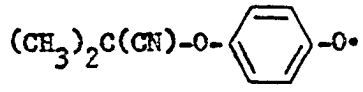


Reaction (1) is hydrogen abstraction from the quinone by the polymer radical, P•. In reaction (2) the hydrogen atom is abstracted from the polymer radical by the quinone. Reaction (3) is addition of the polymer radical to the carbon-carbon double bond. Reaction (4), where the polymer radical is added to the quinone oxygen, is suggested by most recent workers as the most common path of radical attack on quinones. The work of Bickel and Waters[5] shows that the radical produced by the

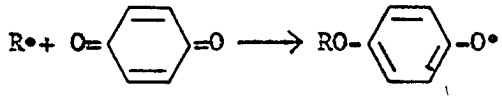
decomposition of azo-isobutronitrile:



reacts with p-benzoquinone to form the radical:



or, more generally



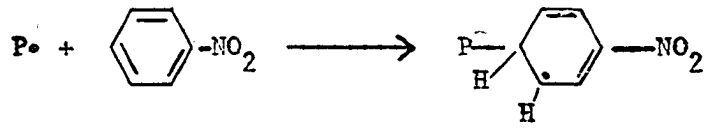
They found no evidence of nuclear substitution in the quinone.

In the benzoyl peroxide initiated polymerization of vinyl acetate, nitrobenzene has been shown to be a weak retarder. Dinitrobenzenes are characteristic of weak inhibitors with an important exception. The final constant slope at the end of the induction period is not the slope of an uninhibited polymerization, but corresponds to the presence of a weak retarder. The dinitro compound, therefore, in the course of stopping chains, yields a product which has a retarding power. Trinitrobenzene is a strong inhibitor for the polymerization of vinyl acetate, but the kinetics of the inhibited polymerization does not appear to apply to moderate or strong inhibition. This was found to be due to the fact that

trinitrobenzene, in the course of stopping two polymer chains, is converted into another inhibitory substance. In this second stage of chain terminating ability, two more chains are stopped, and the nitro compound is converted into a weak retarder.

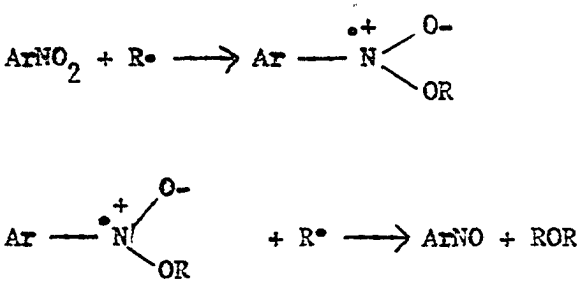
Nitro compounds have a similar effect on the sensitized polymerization of styrene. Again, the reactivity of the nitro compound as a retarder increases sharply with the number of nitro groups. Nitrobenzene is a retarder and trinitrobenzene is a weak inhibitor. During the period of weak inhibition, the product of the radical-trinitrobenzene reaction is converted into a retarder. Nitro compounds have little effect in retarding the polymerization of methyl methacrylate.

Opinions on the mechanism by which nitro compounds inhibit vinyl polymerization can be divided into two groups. Some workers such as Price have considered that the first step in the retardation involves macroradical attack on the aromatic nucleus of the nitro compound, with addition of the radical to the aromatic nucleus.



Their conclusion was supported by the fact that nitrobenzene is a retarder in the polymerization of styrene and nitromethane is an inert solvent. Bartlett and Kwart[1] in their investigation of the effect of nitro compounds on the polymerization of vinyl acetate

supposed that the primary attack takes place on the oxygen atom of the nitro group.



They based their hypothesis on the observation that the retarding powers of the nitro compounds increase markedly with the number of nitro groups. Such a marked increase cannot be explained by a simple substitution reaction taking place at the aromatic nucleus. They supposed that the free radicals attack the oxygen atom of the nitro group, thus depriving one of the nitro groups of its character in the course of the inhibition.

Bevington and Ghanem[7] studied the effect of nitro compounds on the sensitized polymerization of styrene. They established that picric acid does not build in a carbon-carbon bond into the polymer.

Inomoto and Simamura[8] investigated the reaction of 1-cyano-1-methylethyl radical with various nitro compounds. They found that the radical did indeed react with the nitro group. The decomposition of azo-isobutyronitrile in nitrobenzene gave a small amount of hydrogen cyanide, acetone, and N-phenyl-O, N-bis (cyano-1-methylethyl) hydroxylamine. The exact method of attack by the radical is unknown. The radical may abstract the oxygen

atom directly (Reaction 5), or it may add to the oxygen atom and later decompose into a nitroso compound and a 1-cyano-1-methylethoxy radical (Reaction 6).

$$ArNO_2 + (CH_3)_2\underset{\underset{CN}{|}}{C}\bullet \longrightarrow ArNO + (CH_3)_2\underset{\underset{CN}{|}}{CO}\bullet \qquad (5)$$

$$ArNO_2 + (CH_3)_2\underset{\underset{CN}{|}}{C}\bullet \longrightarrow ArN\begin{matrix}\diagup O\bullet \\ \diagdown OC(CH_3)_2CN\end{matrix} \longrightarrow \qquad (6)$$

$$ArNO + (CH_3)_2\underset{\underset{CN}{|}}{CO}\bullet$$

The nitroso compound reacts with two 1-cyano-1-methylethyl radicals to yield a substituted hydroxylamine (Reaction 7).

$$ArNO + 2(CH_3)_2\underset{\underset{CN}{|}}{C}\bullet \longrightarrow Ar\text{-}\underset{\underset{C(CH_3)_2CN}{|}}{N}\text{-}O\text{-}C(CH_3)_2CN \qquad (7)$$

The 1-cyano-1-methylethoxy radicals can give rise to acetone and hydrogen cyanide either through the formation of acetone cyanhydrin (Reaction 8), or through decomposition (Reaction 9).

$$(CH_3)_2\underset{\underset{CN}{|}}{CO}\bullet \xrightarrow[\text{donor}]{\text{hydrogen}} (CH_3)_2\underset{\underset{CN}{|}}{COH} \longrightarrow (CH_3)_2CO + HCN \qquad (8)$$

$$(CH_3)_2\underset{\underset{CN}{|}}{CO}\bullet \longrightarrow (CH_3)_2CO + \bullet CN$$

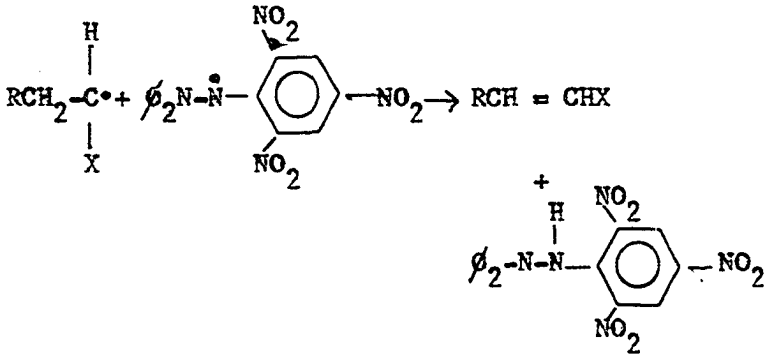
$$\bullet CN \xrightarrow[\text{donor}]{\text{hydrogen}} HCN \qquad (9)$$

Similar results were obtained when 1-cyano-1-methylethyl radicals were reacted with m-dinitrobenzene and tetranitromethane. Nitromethane did not react with this radical.

Inomoto's and Simamura's investigations[8] show that radicals do indeed react with the oxygen atom of the nitro group. In the case of aromatic nitro compounds with a replaceable hydrogen atom in the nucleus, the mechanism postulated by Price[6] cannot be excluded. It is likely that no single mechanism is applicable to all nitro compounds and all radicals.

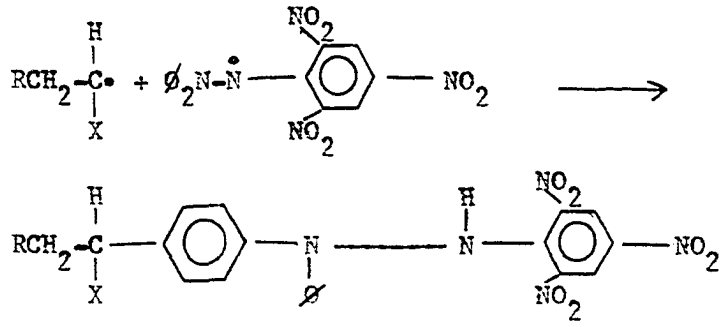
B. Stable Free Radical Terminators

A free radical can be used as an effective terminator if it is stable enough so as not to react with initiator or monomer and initiate polymerization, yet it can react readily with other radicals produced in the system. The stable free radical, 2,2-Diphenyl-1-picrylhydrazyl (DPPH) is often used as an inhibitor to determine the rate of initiation in free radical chain processes. It reacts with other radicals to form nonradical products. The most probable reactions are:



(10)

in which a hydrogen atom is transferred from one radical to another or a combination reaction such as:



(11)

The limitations of the use of DPPH to determine the rate of production of free radicals have been pointed out by Bengough.[9] In the polymerization of vinyl acetate, the product of the reaction of DPPH with other radicals in the system inhibits the polymerization process. Such product inhibition is not unreasonable, since a simple combination or disproportionation reaction involving DPPH would give rise to a picryl group, and it is known that s-trinitrobenzene both inhibits and retards the sensitized polymerization of various monomer systems.

It is expected that a single picryl group would react with a number of free radicals. This would produce an induction period, or decrease the rate of polymerization, much more than expected on the assumption that one free radical reacts with one molecule of DPPH. The polymerization would then proceed at its uninhibited rate, only after all of the nitro compound has been removed from the system.

When methyl methacrylate is polymerized in the presence of

DPPH, the induction period and the rate of polymerization after the induction period are very close to the values expected by assuming one radical reacts with one molecule of DPPH. Kice[10] has shown that the methyl methacrylate radicals do not react appreciably with nitro compounds. This could explain the agreement between the expected and observed values in the DPPH inhibited methyl methacrylate polymerization.

C. Kinetics in Inhibited and Retarded Polymerizations

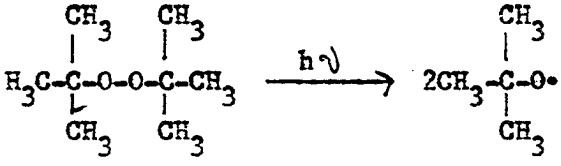
The general kinetic scheme for an inhibited free radical polymerization as proposed by Kice[11] can be given as:

		Rate	
Initiation	$I \xrightarrow{k_d} 2R\cdot$	$2k_d f(I^*)$	(12)
Propagation	$R\cdot + M \xrightarrow{k_p} R\cdot$	$k_p(R\cdot)(M)$	(13)
Addition or Transfer	$R\cdot + X \xrightarrow{k_x} Z\cdot$	$k_x(R\cdot)(X)$	(14)
Copolymerization	$Z\cdot + M \xrightarrow{k_o} R\cdot$	$k_o(Z\cdot)(M)$	(15)
Termination	$Z\cdot + R\cdot \xrightarrow{k_c}$ Inactive Product	$k_c(Z\cdot)(R\cdot)$	(16)
	$Z\cdot + Z\cdot \xrightarrow{k_z}$ Inactive Product	$2k_z(Z\cdot)^2$	(17)
	$R\cdot + R\cdot \xrightarrow{k_t}$ Inactive Product	$2k_t(R\cdot)^2$	(18)

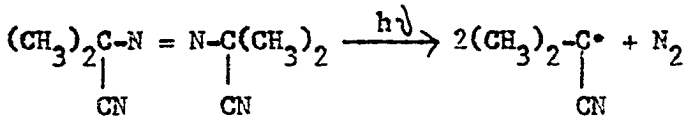
where X is the added terminator and Z• is the radical formed by the reaction of R• with terminator. Z• may be formed either by addition of R• to X or by transfer of an atom or group to R• from X.

Any substance that arrests or retards the polymerization of a vinyl monomer does so by reacting either with initiator or polymer free radical R•, to yield a new radical Z•. In all cases, the reaction between the terminator and a radical competes with one of the normal steps in the polymerization process. The velocity constant for the terminator-radical reaction is dependent on the reactivity of both substances. The magnitude of the effect of the terminator on the polymerization depends not only on the rate of the terminator reaction, but also upon the rate of the normal reaction with which it competes. The effect of a specific terminator, therefore, varies from one monomer system to another.

The initiation reaction (12) is essentially a decomposition reaction in which the sensitizer, usually an azo-isobutyronitrile compound or a peroxide, is exposed to ultraviolet light and decomposes into two free radicals.

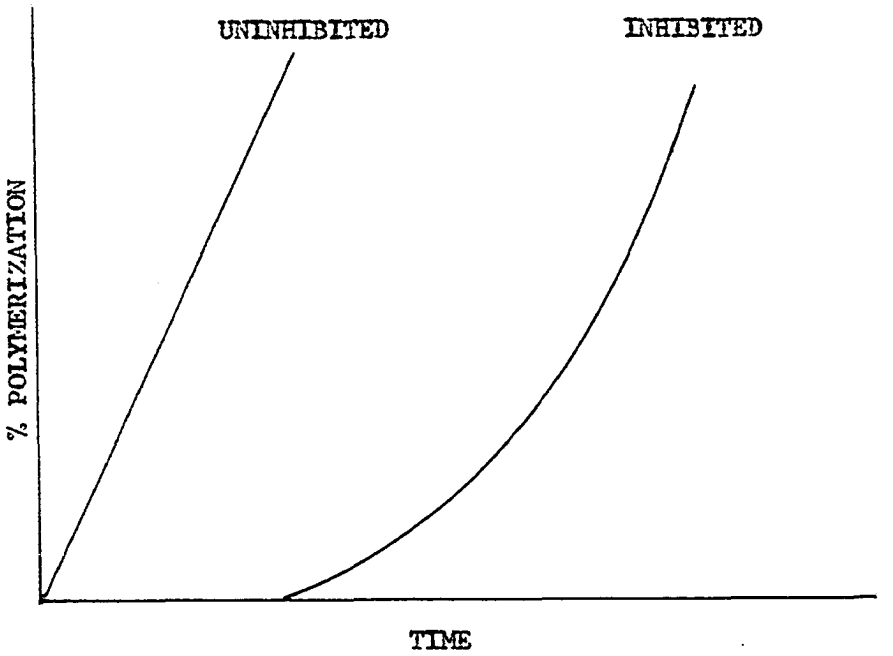


or:



The rate of decomposition is dependent on the rate constant k_d, the intensity of absorbed light, (I*) and the efficiency of initiation, f.

The propagation reaction (13) is in direct competition with reactions involving terminator molecules, (14). Since the monomer concentration is much greater than the inhibitor concentration, k_x must be so much larger than k_p that nearly all the radicals react according to Reaction (14). As the terminator is consumed, the balance between reaction (13) and reaction (14) shifts; more primary radicals are now being captured by monomers and the terminator reacts with polymer radicals containing a small number of monomer units. This is observed in the % polymerization versus time curve as the gradual increase to a rate which is observed in a system in which the termination is absent.



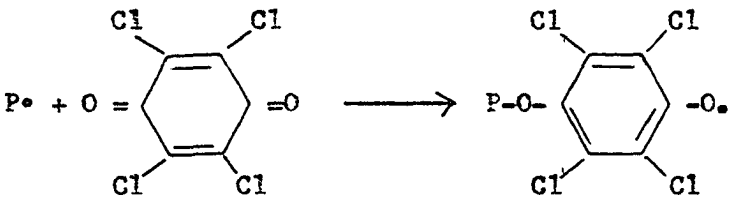
During that time in which the terminator is effective, reaction (17) should be the predominant termination process. If reaction (17) represents coupling, each occurrence will terminate two chains and involve two terminator radicals. If it represents a disproportionation reaction with regeneration of a molecule of terminator, two chains will be ended, but only one inhibitor residue will be consumed.

Reactions (16) and (18) may be neglected because of the concentration sequence $[R\cdot] \ll [Z\cdot] \ll [Z]$ which must apply in a strongly retarded system. As the terminator is consumed, however, the cross termination reaction (16), and the normal termination reaction (18), become increasingly important.

The copolymerization reaction (15) has been shown to be of some importance in the reactions of vinyl compounds with quinones. The magnitude of this effect, however, is dependent on the nature of the monomer and the quinone involved. In the polymerization of styrene in the presence of p-benzoquinone, Bevington et al.,[1] have shown that only low molecular weight polymer is produced in the early stages of the polymerization, and that p-benzoquinone is combined in quantities that are more than one p-benzoquinone unit per polymer molecule, and that a large part of the combined quinone may be removed by a substance which cleaves ether linkages. The removal of quinone is accompanied by a substantial decrease in the average molecular weight of the polymer. In the sensitized polymerization of methyl methacrylate in the presence of C^{14}-para-

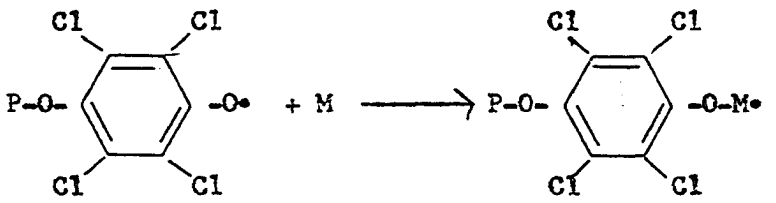
benzoquinone, Bevington et al.,[3] have shown that the number of retarder molecules combined in each polymer molecule increases significantly with the concentration of C^{14}-para-benzoquinone in the polymerizing system.

These copolymerization reactions are very limited in a monomer-para-benzoquinone system. For other quinones, e.g., p-chloranil, copolymerization has been shown to be more pronounced in both a styrene[12] and methyl methacrylate[10] system. It appears that the first stage in the copolymerization reaction is the same for both styrene and methyl methacrylate.



(19)

The product of (19), then, reacts with a monomer molecule so that more than one molecule of chloranil is contained in the polymer. The reaction takes place through the carbonyl groups to give an aromatic-aliphatic polyether.



Kice[10] has shown that with methyl methacrylate 80% of the Z• radicals were being consumed by reaction (15). Breitenbach[12] has shown by chemical degradation that styrene polymerizes with chloranil, yielding essentially a 1:1 copolymer of the two compounds.

II. EXPERIMENTAL

A. Calibration of Dilatometer

The dilatometer is shown in Figure 4. Marks were placed at the tops of both capillaries. The reaction cell was then filled with triple distilled C.P. mercury to a level below the marked lines. The dilatometer was then placed in a constant temperature water bath and allowed to come to equilibrium. The temperature was read with a Parr calorimetric thermometer up to $30.100 \pm .001^{\circ}C$. Once a constant mercury level in the capillaries was achieved, the level and temperature were recorded. The temperature was then advanced at approximately $1^{\circ}C$ intervals, the system was allowed to come to equilibrium, and the new level and temperature were recorded. The same procedure[13] was used in calibrating both dilatometers.

The capillary tubes in dilatometers Number 1 and Number 2 were found to have a radii of 2.613×10^{-2} cm and 2.644×10^{-2} cm, respectively. The reaction cells were found to contain volumes of 32.1703 ml and 31.9923 ml, respectively, at $25^{\circ}C$.

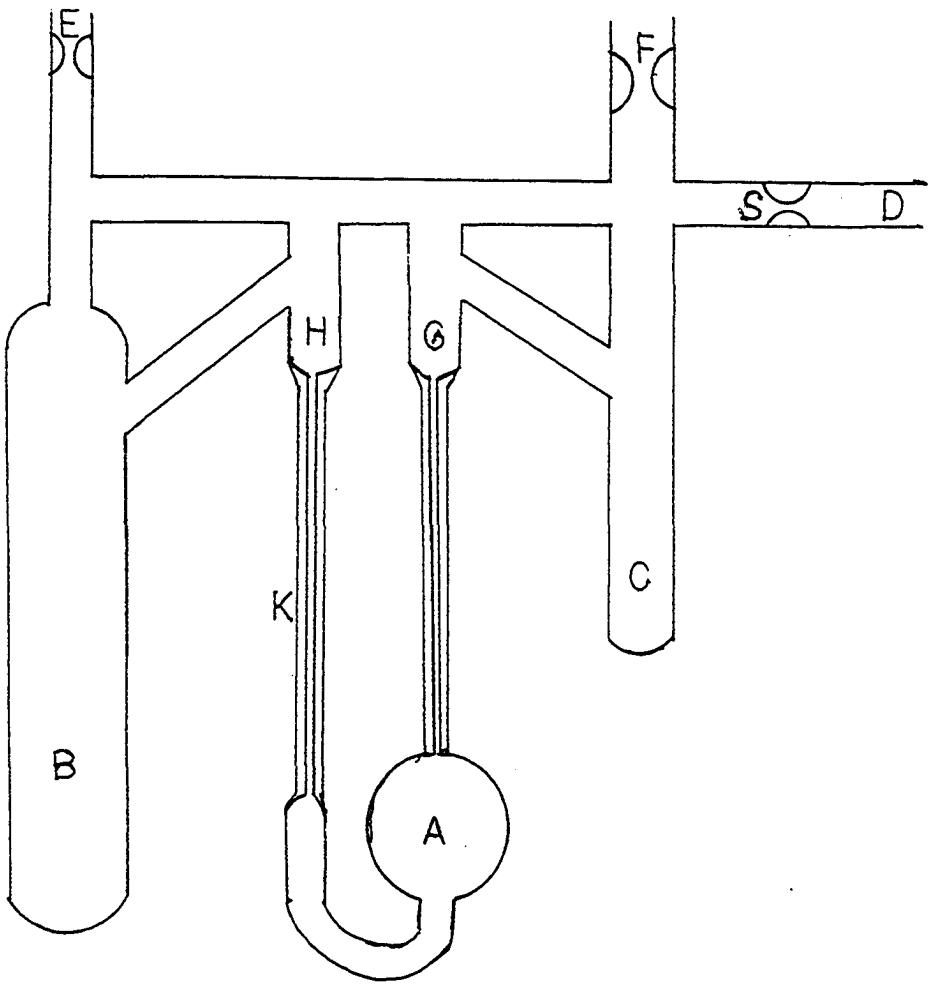


Figure 4: Dilatometer: (A) reaction cell; (B) storage reservoir; (C) inhibitor reservoir

B. Chemicals

1. The α-methylstyrene was obtained from the Dow Chemical Company. The monomer was purified by passing it through a column of activated alumina, followed by distillation in the presence of sodium metal and under a nitrogen atmosphere. The purified monomer was then sparged with nitrogen for ten minutes and stored under refrigeration. The refractive index of the purified monomer was $n_D^{25} = 1.5356 \pm 0.0002$.

2. Di-tert-butyl peroxide (Matheson Coleman and Bell) was used as the initiator. Its purity was found to be $83.0 \pm 0.7\%$ by the iodine liberation process of Mair and Graupner.[14]

3. para-Benzoquinone and p-chloranil were purified with ten passes through a zone refiner with 30% rejection. The zone refined material was then recrystallized from ethanol. The melting points of para-benzoquinone and p-chloranil were 114.5 - 115.0°C and 288 - 290°C, respectively.

4. Duroquinone was recrystallized from ethanol three times. The melting point was 111.0 - 111.5°C.

5. para-Nitrotoluene was purified by ten passes in a zone refiner with 30% rejection. The refined material was then recrystallized from 50% ethanol, melting point 52.5 - 53.0°C.

6. Nitrobenzene was purified by fractional distillation. Refractive index was $n_D^{25} = 1.5560 \pm 0.0001$.

7. ortho-, meta-, and para-Dinitrobenzenes were recrystallized three times from 95% ethanol. The melting points were

117 - 118°C, 89.5 - 90.0°C and 172 - 173°C, respectively.

8. 1,3,5-Trinitrobenzene was recrystallized three times from 95% ethanol. The melting point was 120 - 121°C.

9. 2,2-Diphenyl-1-picrylhydrazyl was used as obtained from the J.T. Baker Chemical Company. It has a stated melting point of 136 - 138°C.

C. Apparatus

1. Two dilatometers, as shown in Figure 4, were used. The capillary tubes in dilatometers Number 1 and Number 2 were found to have average radii of 2.613×10^{-2} cm and 2.644×10^{-2} cm, respectively. The reaction cells were found to contain volumes of 32.1703 ml and 31.9923 ml, respectively, at 25°C when filled to the mark.

2. The cathetometer was manufactured by Griffins and George, Ltd. (London). The brass scale of this instrument was calibrated at 20°C with a coefficient of thermal expansion, α, of 0.000017 $deg.^{-1}$. The scale can be read to 0.001 cm.

3. The thermostatic bath manufactured by the E.H. Sargent Co., had a heater, circulator and controller. (Thermonitor Model ST). The temperature precision in the 25°C region is $\pm$ .01°C.

4. The ultraviolet light source was fitted with a Pyrex filter to cut out shorter wavelengths.

D. Determination of the Rate of Polymerization

A weighed amount of α-methylstyrene and di-tert-butyl peroxide, enough to make a 50 ml 100:1 monomer:initiator mole ratio solution, was placed into the storage reservoir B. (See Figure 4) A weighed amount of inhibitor was also placed in the same storage reservoir. Tubes E and F were sealed with a flame and a vacuum pump was attached at D. The contents of B were then frozen with liquid nitrogen, degassed, and thawed four times, then sealed at S while under vacuum. The dilatometer was then allowed to warm up to room temperature. The contents were mixed by inverting and vigorously agitating the dilatometer. The reaction cell A was then filled by allowing the solution to run into H, down capillary K, until it overflowed into G. By tilting the dilatometer, a meniscus level below the marked lines could be achieved. The dilatometer was then placed into the constant temperature bath at 25°C and allowed to come to equilibrium.

Once a constant liquid level was maintained, the ultraviolet light was turned on and the change in volume was observed with the cathetometer. Readings were taken at ten minute intervals for six hours.

Occasionally the inhibitor was placed in C and degassed separately. This was done periodically to check the uninhibited rate of α-methylstyrene polymerization. In this procedure the reaction cell was filled to a level below the marked lines with the degassed monomer-initiator solution from B. The uninhibited rate

was observed by the method previously described. Once a constant rate was observed, the liquid in the reaction cell was drained back into the storage reservoir B. The inhibitor from C was then allowed to flow into B and the contents were mixed by vigorous agitation. The reaction cell was then filled with the monomer, initiator and inhibitor solution, and the inhibited rate was observed as before.

The initial volume of the reaction solution, V_I, can be calculated from the following known quantities:

h_m = height of the marked line

h_{mx} = maximum height observed after irradiation

h_i = height at time, t_i

V_m = Volume to marked lines

$\triangle V$ = Difference in volume at h_m and h_{mx}

$$= 2\pi r^2 (h_m - h_{mx})$$

$$V_I = V_m - \triangle V$$

The fractional volume change (FVC) is obtained in the following manner:

V_i = Difference in volume at time, t_i

$$= 2\pi r^2 (h_{mx} - h_i)$$

$$FVC = V_i/V_I = 2\pi r^2 (h_{mx} - h_i) / V_I$$

The conversion of monomer to polymer in moles per liter, (CML), is obtained from the fractional volume change, the density and concentration of pure α-methylstyrene and the dilatometric constant. Values for the density and concentration of α-methylstyrene were obtained by a least squares fit (double precision) on a PDP-10 computer:

t in degrees celsius

$$\rho_t = 0.928303 - 8.86486 \times 10^{-4} t - 1.61072 \times 10^{-9} t^2$$

$$\rho_{25} = 0.906141 \ g/cm^3$$

$$\rho_{25} = 0.906141 \ g/cm^3$$

2. Concentration of pure alpha-methylstyrene

$$[M]_t = 7.85568 - 7.50385 \times 10 \ t - 5.510158$$

$$[M]_{25} = 7.66808$$

3. The dilatometric constant:

$$C_D^t = 1 - .897212 \rho_t$$

$C_D^{25} = 0.187$ at 25°C for 100% conversion of monomer to polymer

The conversion of monomer to polymer in moles per liter can now be calculated:

$$CML = [M]_t \times \frac{\Delta V / V_I}{C_d^t}$$

III. RESULTS AND DISCUSSION

A. Limitation of the Dilatometer Technique for Inhibitor Studies of α-Methylstyrene Polymerization

The dilatometric technique for studying the sensitized polymerization of α-methylstyrene affords certain limitations that should be noted. The sensitivity of the dilatometer coupled with the relatively slow free-radical polymerization of α-methylstyrene makes it extremely difficult to obtain accurate data at the beginning of the polymerization.

When the ultraviolet light was switched on, there was a volume increase observed as an immediate rise in capillary height. The magnitude of this capillary rise varied from less than 0.1 cm for pure monomer to 1.9 cm when 2,2-diphenyl-1-picrylhydrazyl was present in the system.

When the temperature of the water bath was followed, using a Parr Calorimetric thermometer, it was found that the temperature did not vary more than $\pm$ .004°C during the entire polymerization of α-methylstyrene in the presence of 2,2-diphenyl-1-picrylhydrazyl. It was also observed that there was no notable temperature change when the ultraviolet light was switched on, although there was a marked volume increase. When the ultraviolet light was turned off during the polymerization, there was a corresponding volume decrease. The volume increased again, however, when the

ultraviolet light was turned on. Again, there was no notable temperature difference when the ultraviolet light was on or off.[15]

Because of the relatively slow polymerization of ∝-methylstyrene, compared to other monomers, any factor that influences the meniscus levels in the capillaries is hard to overcome by polymerization.

The dilatometer technique, however, because it allows for a point to point following of the polymerization curve at very low degrees of conversion of monomer to polymer, is still the best method for inhibitor studies.

B. Effect of p-Benzoquinone on the Sensitized Polymerization of ∝-Methylstyrene

The effect of p-benzoquinone on the sensitized polymerization of ∝-methylstyrene can be seen in Figure 5. The conversion of monomer to polymer in moles per liter (CML) is plotted versus time for three concentrations of p-benzoquinone: 1.5×10^{-3}, 3.0×10^{-3}, and 6.0×10^{-3} M/l. As can be seen from the plot, there is no induction period and p-benzoquinone appears to be a retarder.

The color of the monomer-initiator-p-benzoquinone solutions were various degrees of yellow, darker yellow at higher p-benzoquinone concentrations. The yellow color gradually decreased during the polymerization process. At the end of the polymerization, the solutions were colorless, except when the initial concentration was 6.0×10^{-3} M/l, then a slight yellow color still existed.

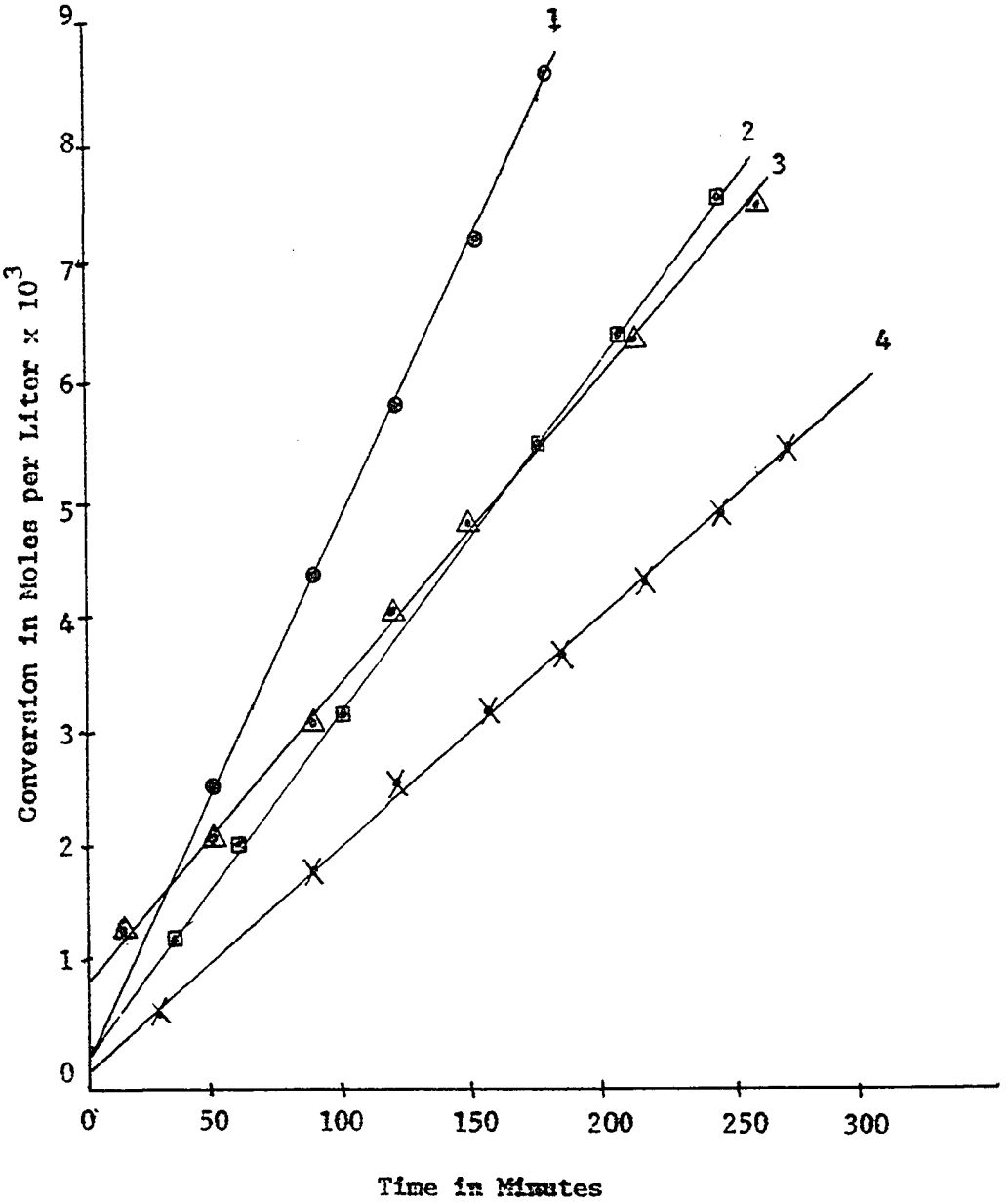


Figure 5: Conversion-time plots for experiments involving α-methylstyrene; di-tert-butyl peroxide and benzoquinone. The numbers correspond to benzoquinone concentrations of: (1) 0; (2) 1.5 x 10^{-3}; (3) 3 x 10^{-3}; (4) 6 x 10^{-3} moles per liter. Monomer:initiator mole ratio 100:1.

C. The Effect of p-Chloranil and Duroquinone on the Sensitized Polymerization of ∝-Methylstyrene

Duroquinone and p-chloranil and discussed together in this section because of their similar effect on the polymerization of ∝-methylstyrene. Neither of the compounds inhibited or suppressed the rate of polymerization. (See Figures 6 and 7)

It has been reported that p-chloranil copolymerized[12] with both methyl methacrylate and styrene. If p-chloranil behaves similarly with ∝-methylstyrene, this could explain p-chloranil's lack of an inhibitory effect.

Duroquinone has been reported to be an inhibitor for the benzoyl peroxide initiated polymerization of vinyl acetate.[2] Figure 6, however, shows that duroquinone has no terminating effects on the polymerization of ∝-methylstyrene.

As with p-benzoquinone, the monomer-initiator-inhibitor solutions of p-chloranil and duroquinone were various degrees of yellow, depending on the concentrations. The yellow color gradually decreased and eventually disappeared during the course of the reaction. Only at the highest initial concentrations (6×10^{-3} M/l) did a faint yellow color exist at the end of the polymerizations.

D. The Effect of Nitrobenzene and p-Nitrotoluene on the Sensitized Polymerization of ∝-Methylstyrene

Figure 8 shows the results of the polymerization of ∝-methylstyrene in the presence of nitrobenzene and p-nitrotoluene. Both

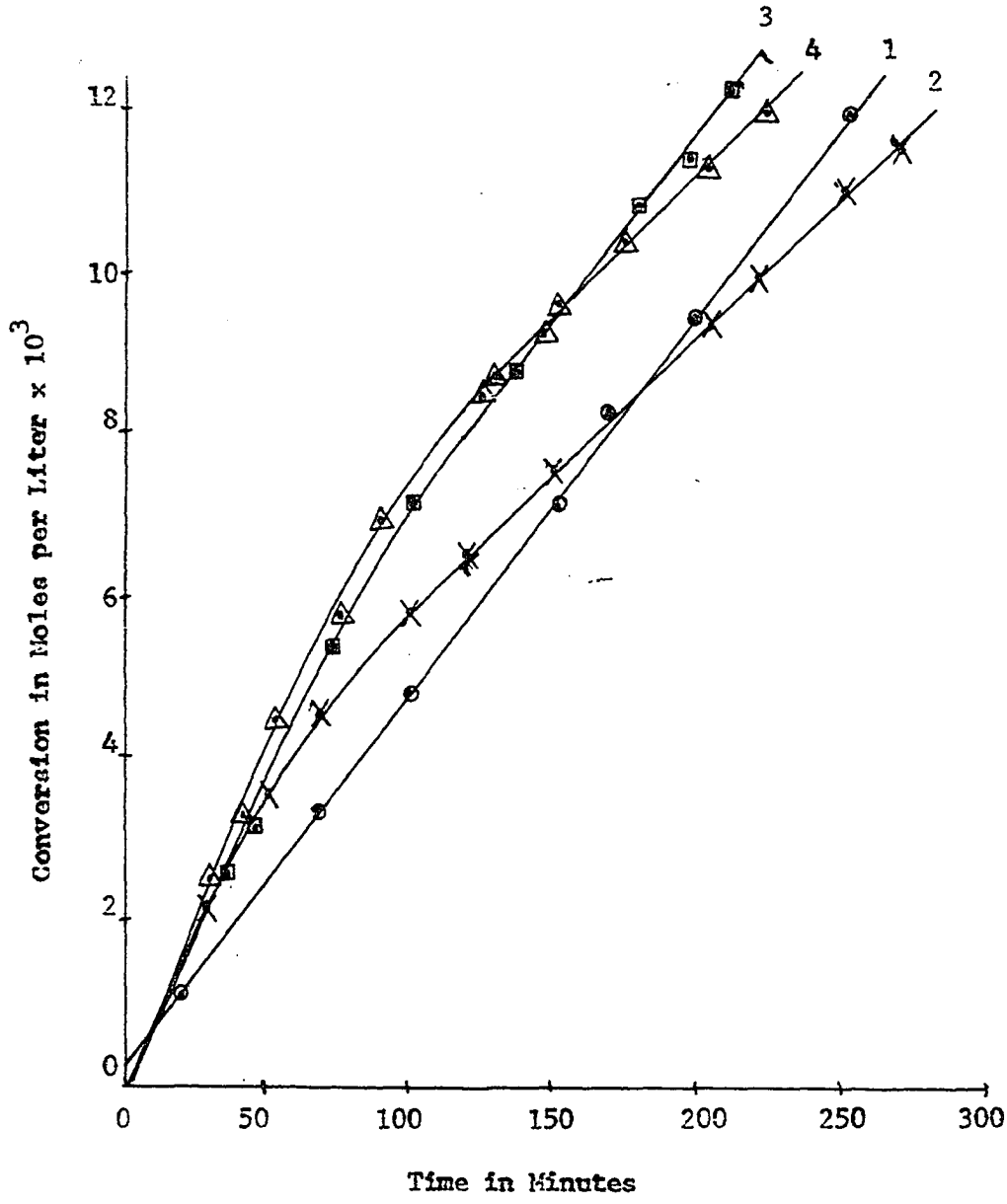


Figure 6: Conversion-time plots for experiments involving α-methylstyrene; di-tert-butyl peroxide and duroquinone. The numbers correspond to duroquinone concentrations of: (1) 0; (2) 1.5 x 10^{-3}; (3) 3 x 10^{-3}; (4) 6 x 10^{-3} moles per liter. Monomer: initiator mole ratio 100:1.

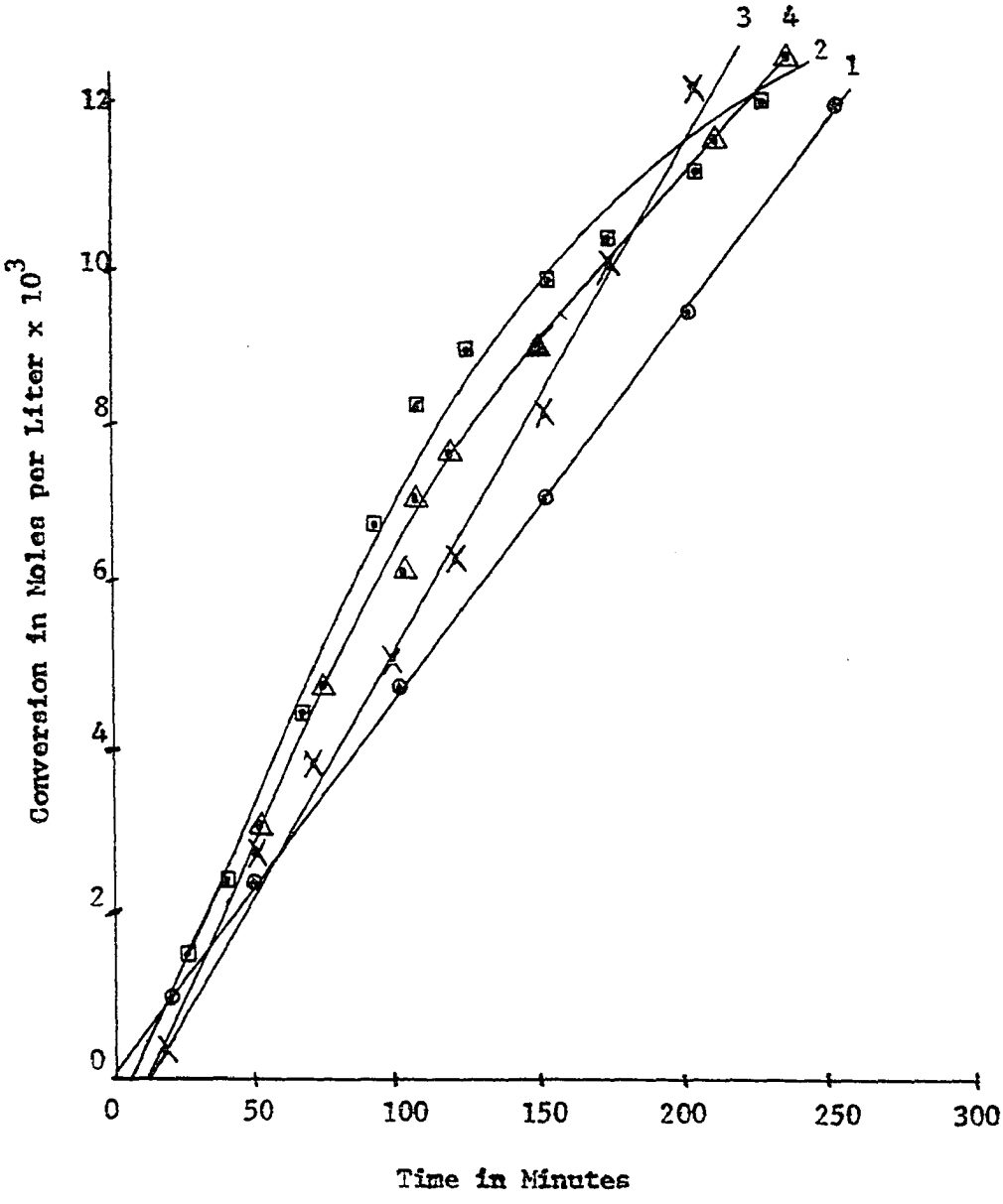


Figure 7: Conversion-time plots for experiments involving ∝-methylstyrene; di-tert-butyl peroxide and chloranil. The numbers correspond to chloranil concentration of: (1) 0; (2) 1.5 x 10^{-3}; (3) 3 x 10^{-3}; (4) 6 x 10^{-3} moles per liter. Monomer: initiator mole ratio 100:1

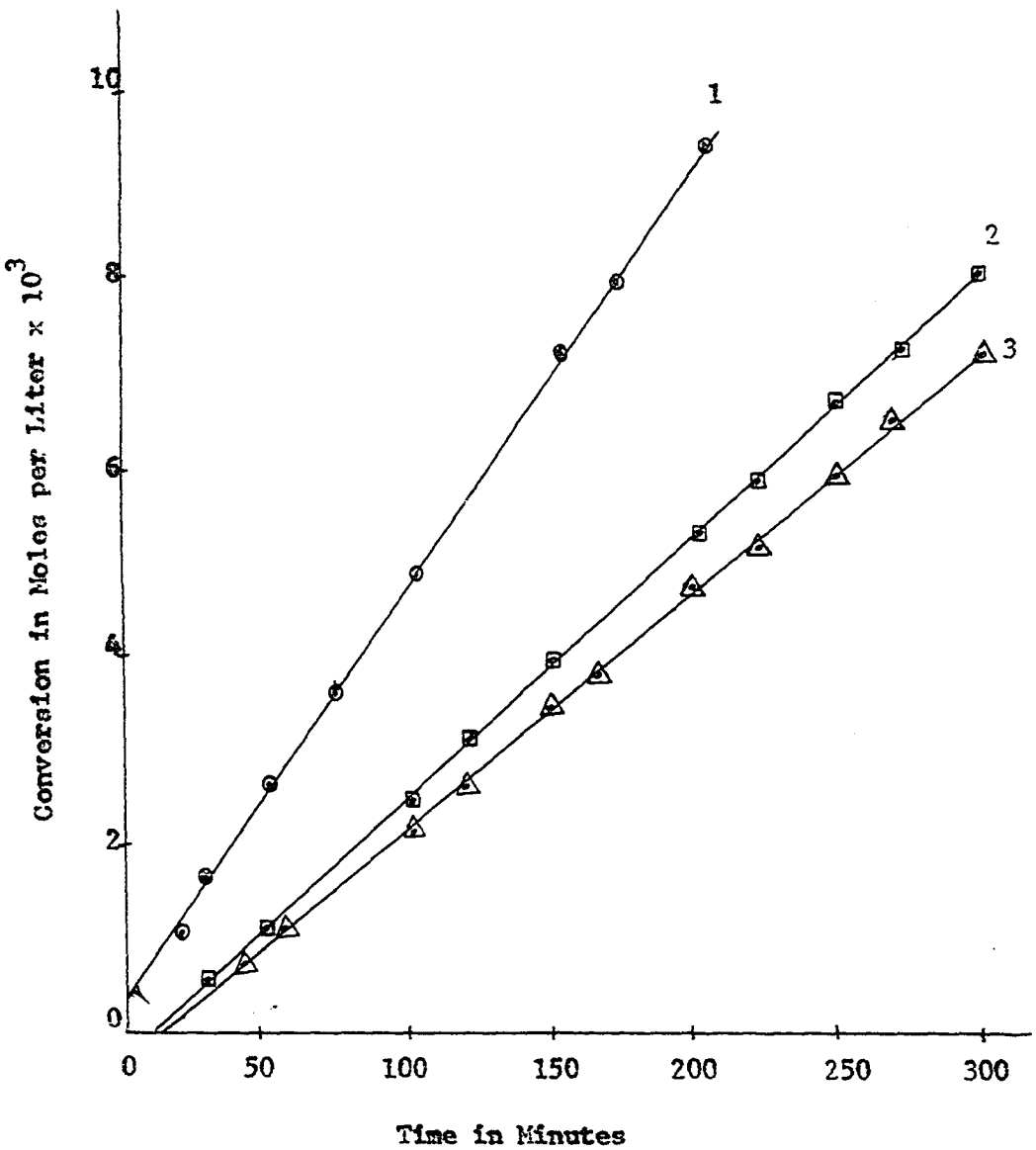


Figure 8: Conversion-time plots for the polymerization of α-methylstyrene in the presence of nitrobenzene and para-nitrotoluene. The numbers correspond to: (1) uninhibited; (2) 3.1×10^{-3} M/l nitrobenzene; (3) 2.8×10^{-3} M/l para-nitrotoluene. Monomer: initiator mole ratio 100:1.

compounds can be classified as retarders for this system.

The monomer-initiator-inhibitor solutions were colorless at the beginning of the polymerization. The nitrobenzene solution remained colorless throughout the polymerization. The p-nitrotoluene solution, however, was a light pink in color following the polymerization period.

E. The Effect of Dinitrobenzenes on the Sensitized Polymerization of ∝-Methylstyrene

Figure 9 shows the effect of ortho, meta and para dinitrobenzene on the sensitized polymerization of ∝-methylstyrene.

meta and para-Dinitrobenzene appear to inhibit the polymerization for a short time, after which the polymerization proceeds at a retarded rate.

ortho-Dinitrobenzene completely suppresses polymerization for the entire length of the experiment. With all dinitrobenzenes, the monomer-initiator-inhibitor solutions were colorless before the polymerization. During the polymerization process, the color gradually changed to a light yellow color.

F. The Effect of 1,3,5-Trinitrobenzene on the Sensitized Polymerization of ∝-Methylstyrene

As can be seen from Figure 10, trinitrobenzene is a retarder for the sensitized polymerization of ∝-methylstyrene. It is a stronger retarder than either nitrobenzene or the meta and para-dinitrobenzenes. It is not, however, as effective a terminator as

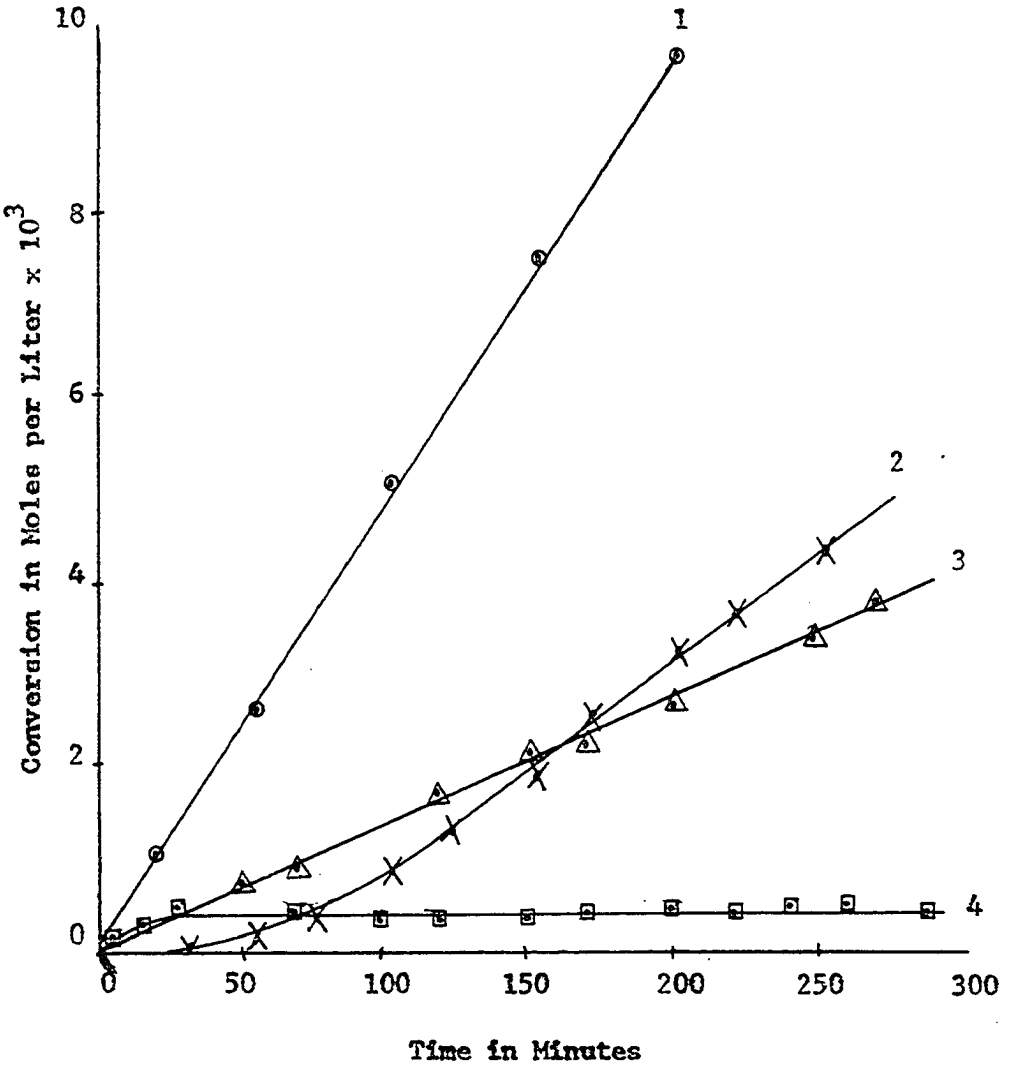


Figure 9: Conversion-time plots for the polymerization of ∝-methylstyrene in the presence of 3 x 10^{-4} moles per liter dinitrobenzenes. The numbers correspond to: (1) uninhibited; (2) meta-dinitrobenzene; (3) para-dinitrobenzene; (4) ortho-dinitrobenzene. Monomer:initiator mole ratio 100:1.

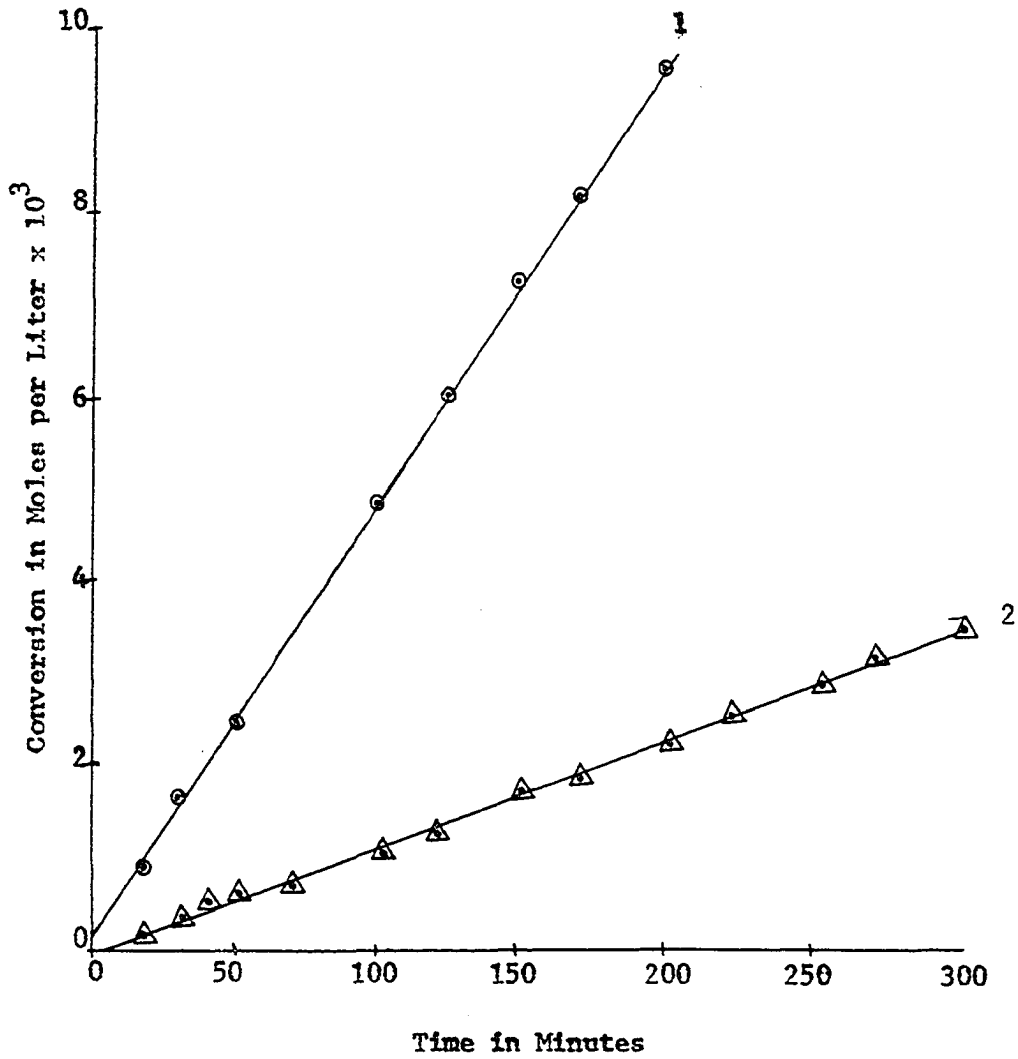


Figure 10: Conversion-time plots for experiments involving ∝-methylstyrene: di-tert-butyl peroxide and 1,3,5-trinitrobenzene. The numbers correspond to trinitrobenzene concentrations of: (1) 0; (3) 2.7×10^{-4} moles per liter. Monomer:initiator mole ratio 100:1.

ortho-dinitrobenzene.

The monomer solution was colorless at the beginning of the polymerization and became a dark yellow color after the six hour polymerization process.

G. The Effect of 2,2-Diphenyl-1-Picrylhydrazyl on the Sensitized Polymerization of ∝-Methylstyrene

The effect of 2,2-diphenyl-1-picrylhydrazyl on the sensitized polymerization of ∝-methylstyrene can be seen in Figure 11. A definite induction period could not be achieved with this stable-free radical. There is a retardation, characteristic of the poly-nitro compounds. Any attempt to increase the concentration of DPPH, in the hope of producing an induction period, resulted in a stronger retardation.

A solution of DPPH in ∝-methylstyrene shows a deep purple, permanganate like color. During the course of the polymerization, the color gradually changed to dark yellow, characteristic of a poly-nitro compound.

Nitro compounds appear to be such strong retarders for the polymerization of ∝-methylstyrene that the use of DPPH as a radical counter would be prohibited.

H. Complex Formations

The possibility of the terminator forming a complex with either the monomer or initiator was considered. In the event that there was a complex formation, the effective concentration of the

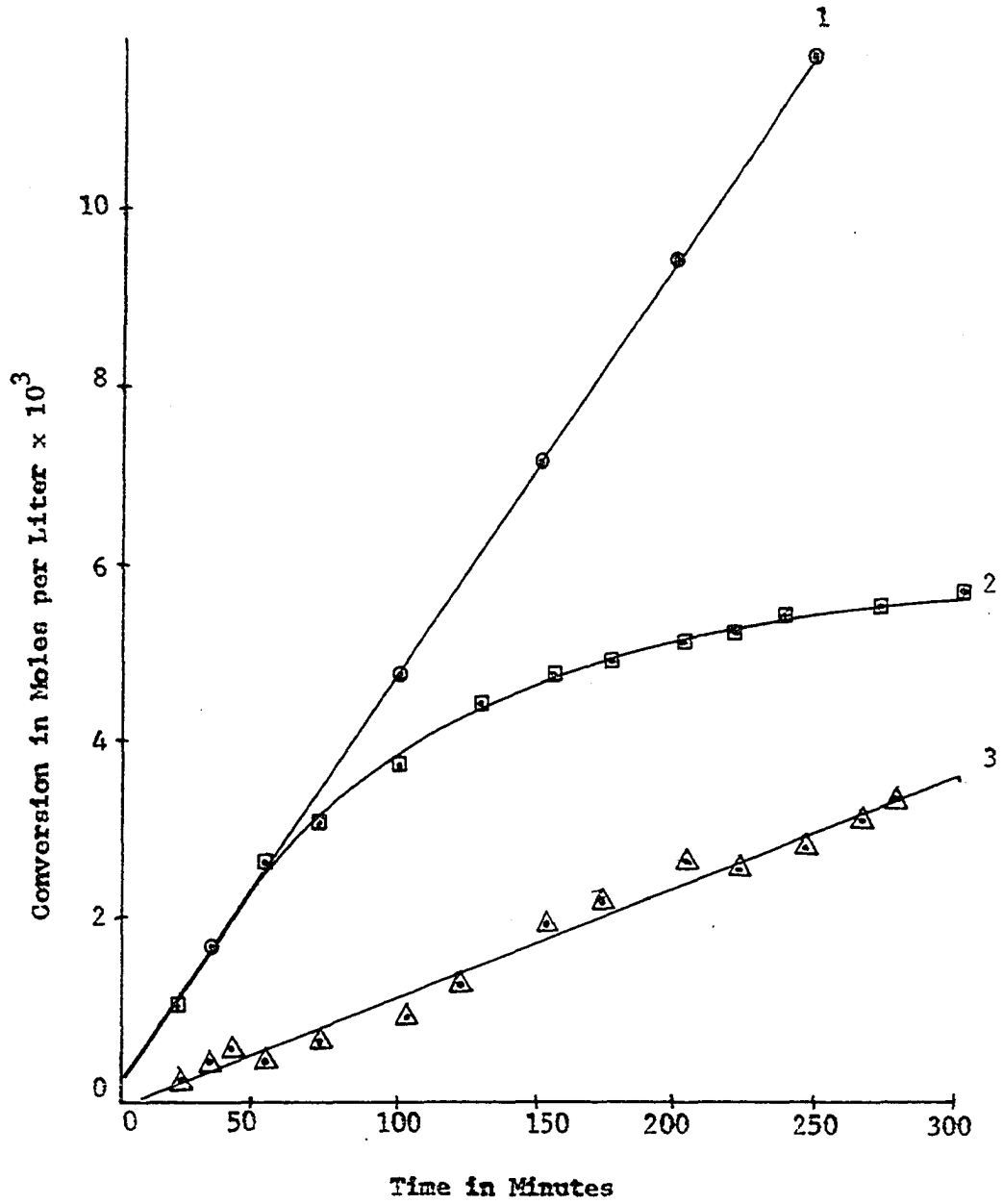


Figure 11: Conversion-time plots for experiments involving ∝-methylstyrene; di-tert-butyl peroxide and 2,2-diphenyl-1-picrylhydrazyl concentrations of: (1) 0; (2) 3 x 10^{-4}; (3) 5 x 10^{-4} moles per liter. Monomer:initiator mole ratio 100:1.

terminator would be changed, thereby altering its terminating powers. Ultraviolet spectra were run on terminator-α-methylstyrene and terminator-di-tert-butyl peroxide solutions to test for the presence of complexes. No complex formations were found in the terminator concentration ranges used in this work.

IV. SUMMARY AND CONCLUSION

1. The effect of quinones, nitro-aromatic compounds, and free radical terminators on the sensitized polymerization of ∝-methylstyrene at 25°C was studied dilatometrically.

2. para-Benzoquinone retards the free radical polymerization of ∝-methylstyrene, while p-chloranil and duroquinone show little or no retarding powers. Thus, the polymerization of ∝-methylstyrene in the presence of p-benzoquinone is more like that of methyl methacrylate than of styrene.

3. Nitrobenzene and p-nitrotoluene are retarders for the free radical polymerization of ∝-methylstyrene, just as they are for styrene and vinyl acetate polymerizations.

4. meta-Dinitrobenzene, para-dinitrobenzene and 1,3,5-trinitrobenzene show a weak inhibition, followed by retardation, in the free-radical polymerization of ∝-methylstyrene.

5. ortho-Dinitrobenzene completely suppressed the free-radical polymerization of ∝-methylstyrene for the entire length of the experiment. (six hours)

6. The poly-nitro group in the stable free radical 2,2-diphenyl-1-picrylhydrazyl has such a retarding effect on the polymerization of ∝-methylstyrene that the use of this stable free-radical as a radical counter in this system would be prohibited. No induction period was observed with DPPH.

7. No terminator-monomer or terminator-initiator complexes could be determined by ultraviolet spectroscopy.

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