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Kinetics of Free Radical-Initiated Polymerization of α -Methylstyrene in the Region of the Ceiling Temperature

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KINETICS OF FREE RADICAL-INITIATED
POLYMERIZATION OF α -METHYLSTYRENE
IN THE REGION OF THE CEILING TEMPERATURE

by

Fred E. Huang

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
April, 1972

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I. INTRODUCTION

This work involved a study of the kinetics of free radical-initiated polymerization of α -methylstyrene. The main purpose was to elucidate the mechanistic features of reversible polymerization. α -Methylstyrene was selected for this work because its reversibility in polymerization results in a low ceiling temperature and also because its kinetic rate constants in polymerization were still unknown.

A. Background

The existence of a ceiling temperature, defined as the equilibrium temperature of the polymerization process, i.e., $\Delta G_p = 0$, was first recognized by Snow and Frey in their study of the copolymerization of olefin with sulfur dioxide in 1938 (1). There have since been reports which show its significance in free radical-initiated vinyl polymerization (2).

The equilibrium state of polymerization can be treated in terms of a simple thermodynamic equilibrium. Thus,

$$-RT \ln K_p = \Delta G_p^\circ$$

where ΔG_p° is the standard state free energy change of the polymerization, and K_p is the equilibrium constant. At the ceiling temperature, T_c ,

$$\Delta H_p - T_c \Delta S_p = \Delta G_p$$

or

$$T_c = \frac{\Delta H_p}{\Delta S_p^\circ + R \ln[M]}$$

where $[M]$ is the equilibrium monomer concentration, defined at standard state of one mole per liter.

Having values of ΔH_p (heat of polymerization determined calorimetrically), T_c can be calculated if the entropy change of polymerization at standard state, ΔS_p° is known. Calculated ceiling temperatures for various polymerization reactions of undiluted monomers are listed in Table 1 (3). Compared with other monomers, the ceiling temperature of α -methylstyrene, 61°C (4), is relatively low. It was once thought that it could not be polymerized by a free radical mechanism. The feasibility of free radical-initiated polymerization was demonstrated by Lowry in 1958 (5). However, the kinetic properties are still little known.

We studied the rate of polymerization of α -methylstyrene dilatometrically over a temperature range from 10 to 70°C . The rate of volume change of polymerizing monomer solution was measured with a cathetometer. The rate of initiation was to be obtained by deliberately adding a free radical scavenger, benzoquinone, to the polymerization system.

B. Kinetics and Mechanism of Free Radical-Initiated Polymerization of α -Methylstyrene

The mechanism of free radical polymerization of α -methylstyrene follows the steps of initiation, propagation, and termination as suggested by Flory (6) in 1957. The free radicals having unpaired electrons can be generated by thermal or photochemical decomposition. The thermal decomposition of an organic molecule

Table 1

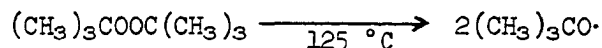
Calculated ceiling temperatures^a

<u>Monomer</u>	<u>$-\Delta H_p^\circ$ (Kcal./mole)</u>	<u>Temp. ($^\circ\text{C}$)</u>
Styrene	16.7	346
Ethylene	22.3	553
Vinyl acetate	21.3	517
Acrylonitrile	17.3	367
Methyl acrylate	18.7	420
Methyl methacrylate	13.0	210
Isobutylene	12.8	200
Vinylidene chloride	14.4	261
α -Methylstyrene	9.0	61 ^b

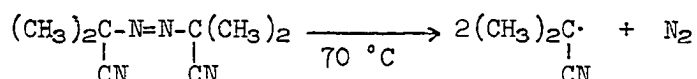
a. Calculated on the assumption that $-\Delta S_p^\circ = 27$ e.u. in each case (see Ref. 3).

b. Calculated value is 60°C (see Ref. 4 and 15).

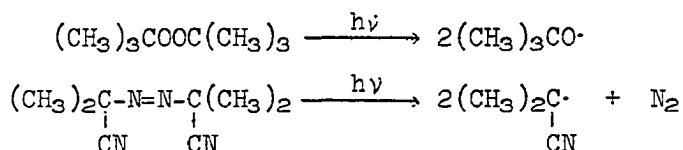
containing a peroxide linkage probably is the most common radical-producing reaction. For example, di-tert-butyl peroxide decomposes at temperatures around 125 °C yielding two tert-butoxy radicals per molecule:



Other peroxide compounds that are often used to produce free radicals on thermolysis are diacetyl peroxide, benzoyl peroxide, and tert-butyl peracetate. Thermolysis of α,α' -azobisisobutyronitrile at about 70 °C yielding a molecule of nitrogen and two isobutyronitrile radicals, is also commonly used:

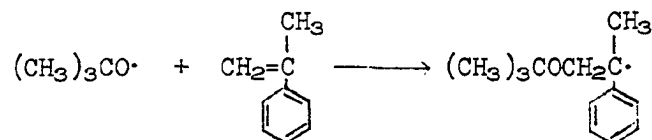


Many compounds are capable of absorbing light and undergoing photochemical decomposition yielding free radicals. Those most commonly used to produce radicals for polymerization are di-tert-butyl peroxide and α,α' -azobisisobutyronitrile. These two compounds decompose at almost any temperature when exposed to ultraviolet light:

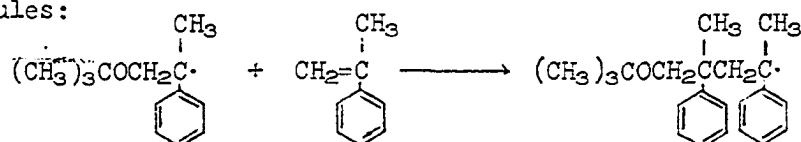


When free radicals are generated in the presence of vinyl monomer, a radical adds to the double bond of the vinyl monomer molecule and generates another radical. This chain reaction of generation of radicals characterizes the free radical-initiated polymerization. For example, a tert-butoxy radical adds to the

exocyclic double bond of α -methylstyrene, forming a chain radical:

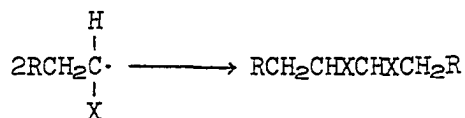


The chain radical formed in the initiation step is then capable of propagating the radical chain by the addition of successive monomer molecules:

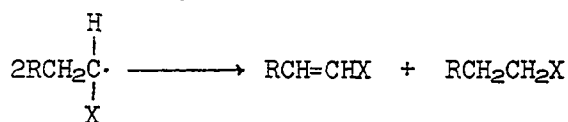


Once the propagation proceeds, the depropagation reaction may occur. Depropagation is the reverse reaction of propagation. For α -methylstyrene, the depropagation plays an important role during polymerization even at room temperature; a relatively low ceiling temperature results, as mentioned (see Table 1). In fact, the ceiling temperature means the temperature where propagation and depropagation proceed at the same rate.

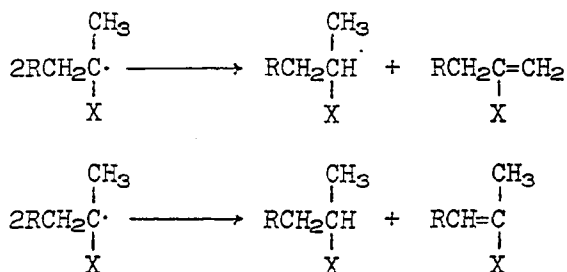
There are two mechanisms possible for termination, namely, combination and disproportionation. The combination mechanism involves the coupling of two radicals by a covalent sigma bond to form one molecule:



In the case of disproportionation, a hydrogen atom is transferred from one radical to another, resulting in the oxidation of one and the concurrent reduction of the other:



Studies (7) have shown that polystyrene terminates predominately by combination, whereas poly(methyl methacrylate) terminates entirely by disproportionation at polymerization temperatures above 60 °C, and partly by each mechanism at lower temperatures. Bevington et al. (7) suggested that this may be due in part to the fact that five hydrogen atoms are available for the disproportionation of poly(methyl methacrylate) radicals:



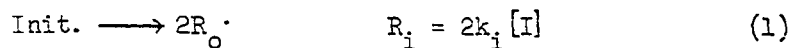
where X represents $-\overset{\text{O}}{\text{C}}-\text{O}-\text{CH}_3$. In the polystyrene radical, $\text{RCH}_2\overset{\text{H}}{\underset{\text{C}_6\text{H}_5}{\text{C}}}\cdot$, only two atoms can take part in the reaction.

Another factor is that the product by combination is sterically strained. Monomers, like α -methylstyrene, that exhibit low ceiling temperature commonly are sufficiently bulky that we expect termination by combination to be sterically unfavorable. So we conclude that the mechanism of termination for α -methylstyrene probably is a disproportionation reaction.

The proposed polymerization mechanism and the corresponding

kinetic expressions can be written as follows:

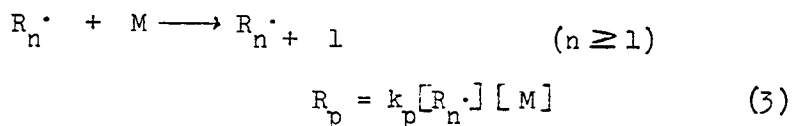
Initiation:



Radical chain formation:

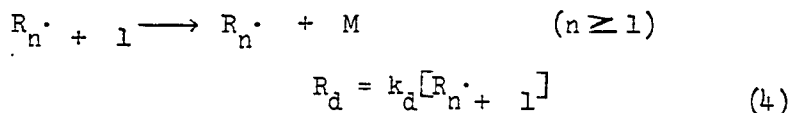


Propagation:

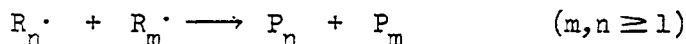


where $R_n \cdot$ is the radical with n repeating monomer units.

Depropagation:



Termination:



where P_n represents a polymer with n repeating monomer units.

$$R_t = 2k_t [R_n \cdot] [R_m \cdot] \quad (5)$$

If equations (1) through (5) are written using $\sum [R_i \cdot] = [R \cdot]$ as was done by Dainton and Ivin (8), then

$$\text{Initiation: } R_i = 2k_i [I] \quad (1)$$

$$\text{Chain radical formation: } R_c = k_c [R \cdot] [M] \quad (2')$$

$$\text{Propagation: } R_p = k_p [R \cdot] [M] \quad (3')$$

$$\text{Depropagation: } R_d = k_d [R \cdot] \quad (4')$$

$$\text{Termination: } R_t = 2k_t [R \cdot]^2 \quad (5')$$

Assuming steady state, $R_i = R_t$, then

$$\begin{aligned}
 [R\cdot] &= k_i^{1/2} [I]^{1/2} / k_t^{1/2} \text{ and} \\
 R &= -d[M]/dt = (k_p[M] - k_d) [R\cdot], \\
 &\quad \text{if } k_p \geq k_d \\
 &= (k_p[M] - k_d) R_i^{1/2} / \sqrt{2} k_t^{1/2}
 \end{aligned} \tag{6}$$

The expected rate of polymerization according to equation (6) is shown in Figure 1. However, equation (4') should read $R_d = k_d([R\cdot] - [R_1\cdot])$, because the smallest radical is incapable of depropagation. This correction is considered important, since in a polymerization involving only equations (1), (2), and (5) the concentration of $R_1\cdot$ is larger than that of any other $R_i\cdot$. When depropagation occurs, $[R_1\cdot]$ becomes an even more significant consideration. Thus, the modified over-all rate of polymerization will be:

$$R = k_p [R\cdot] [M] - k_d ([R\cdot] - [R_1\cdot]) \tag{6'}$$

Let $\alpha = [R_1\cdot] / \sum [R_i\cdot]$, then

$$R = R_i^{1/2} / \sqrt{2} k_t^{1/2} \{ k_p [M] - (1 - \alpha) k_d \} \tag{6''}$$

If $K_p = k_p / k_d = \exp(\Delta S^\circ / R) \exp(-\Delta H^\circ / RT)$, then

$$k_d = k_p \exp(-\Delta S^\circ / R) \exp(\Delta H^\circ / RT)$$

So
$$R = \frac{R_i^{1/2} k_p k_t^{-1/2}}{\sqrt{2}} \{ [M] - (1 - \alpha) \exp(-\Delta S^\circ / R) \exp(\Delta H^\circ / RT) \} \tag{7}$$

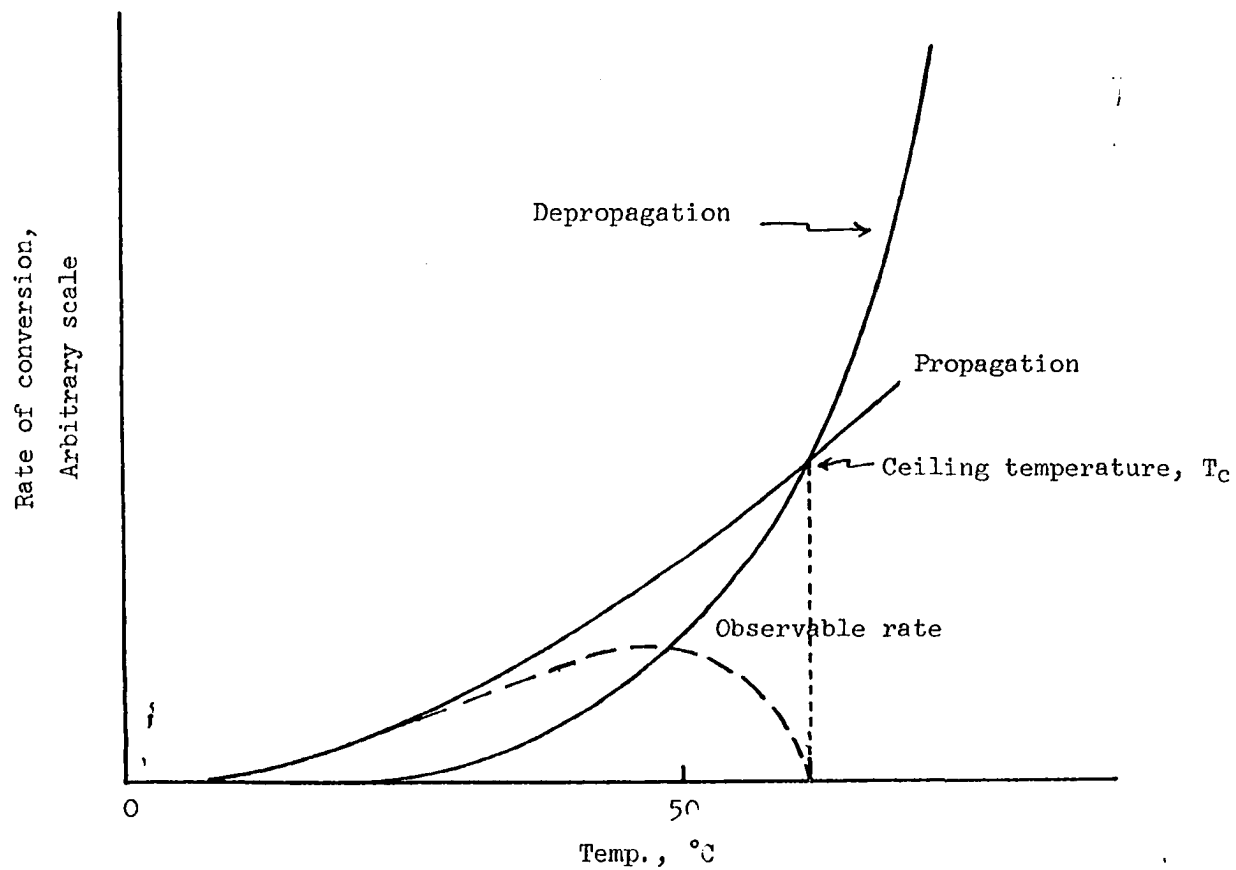


Figure 1. Theoretical plot for eq. 6
(Rate of conversion vs. temperature)

II. EXPERIMENTAL

A. Materials

1. α -Methylstyrene monomer was obtained from The Dow Chemical Company. This monomer, with a stated purity of 99.3%, was first purified by passing it through a column filled with activated alumina to remove the inhibitors if any. It was then transferred into a three-neck, round bottom flask in a distillation system. The monomer was then distilled in the presence of fresh sodium metal and under a nitrogen flow to remove the residual inhibitors and other impurities. A boiling point of 165.4 °C was obtained under atmospheric pressure of about 740 mm. Hg (literature value: 165.74 °C, 1 atm.) (9). The distillate collected showed a refractive index of 1.5355 at 25 °C (literature value: 1.5386 at 25 °C) (10). This monomer was then sparged with nitrogen for ten minutes and stored under refrigeration.

2. Di-tert-butyl peroxide (Matheson Coleman and Bell) was used as initiator. Its purity was found to be 87.4% by iodine liberation process (see "Determination of Purity of Di-tert-butyl Peroxide" section) (11).

3. Benzoquinone (Matheson Coleman and Bell) was purified by sublimation using a cold-finger and vacuum system (Figure 2). The sublimate was then scraped off into a container. The melting point was found to be 115.5 \pm .1 °C (literature value: 115.7 °C) (12).

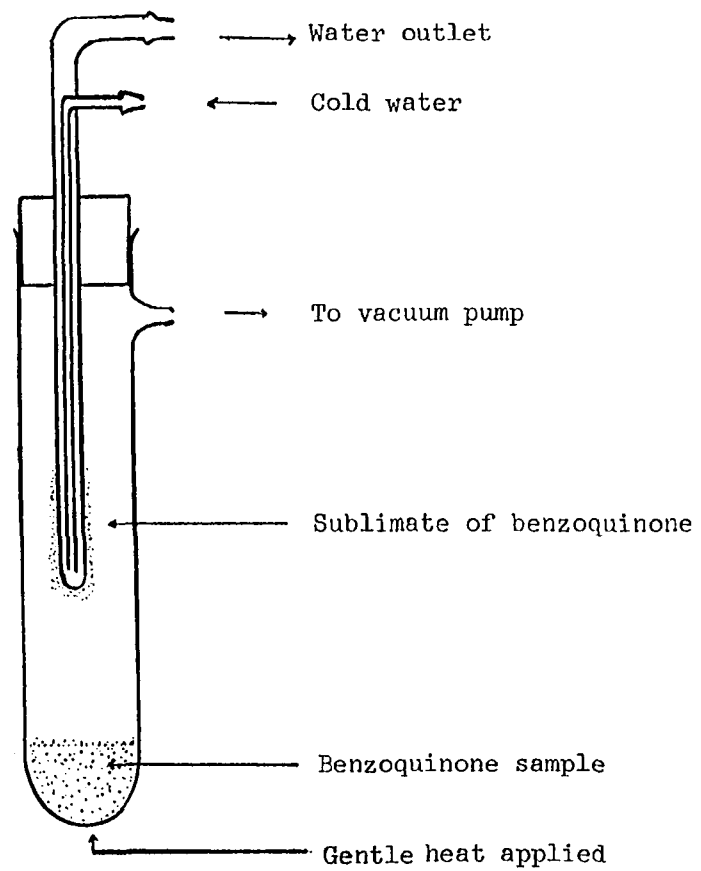


Figure 2. Sublimation system for benzoquinone

B. Apparatus

1. A dilatometer, shown in Figure 3, consists of the reaction cell, A, with a volume about 32 ml., the monomer solution container, D, and two capillary tubes, E and F, with inner radii of 2.611×10^{-2} cm. The dilatometer was cleaned first by introducing a total volume of 15 ml. concentrated nitric acid into A and D, then about 3 drops of 95% ethanol was added to A and D, respectively. The dilatometer was cleaned as the violent oxidation reaction took place. This dilatometer was then rinsed with distilled water four or five times and dried in an oven.

2. A cathetometer manufactured by Griffins and George Ltd., (London) was used. This instrument has a brass scale which has been calibrated at 20 °C with a coefficient of thermal expansion of $.000017 \text{ deg.}^{-1}$. The scale can be read to $\pm .001$ cm.

3. A thermostatic bath with a heater, a circulator and a controller (Thermonitor Model ST) was obtained from E.H. Sargent Co. The temperature control precision is $\pm .01$ °C over the range 10 to 35 °C; and $\pm .05$ °C from 40 to 70 °C.

C. Calibration of Dilatometer

On capillary E of the dilatometer, a base line was marked. Then the reaction cell A, was filled with triple-distilled C.P. mercury to a level below the marked line (the mercury used was from Wood Ridge Chemical Corp.). The dilatometer was then immersed in the thermostat at 25 °C. The uncertainty of temperature reading

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A. Reaction bulb B,C. Openings D. Monomer solution container
 E,F. Capillaries

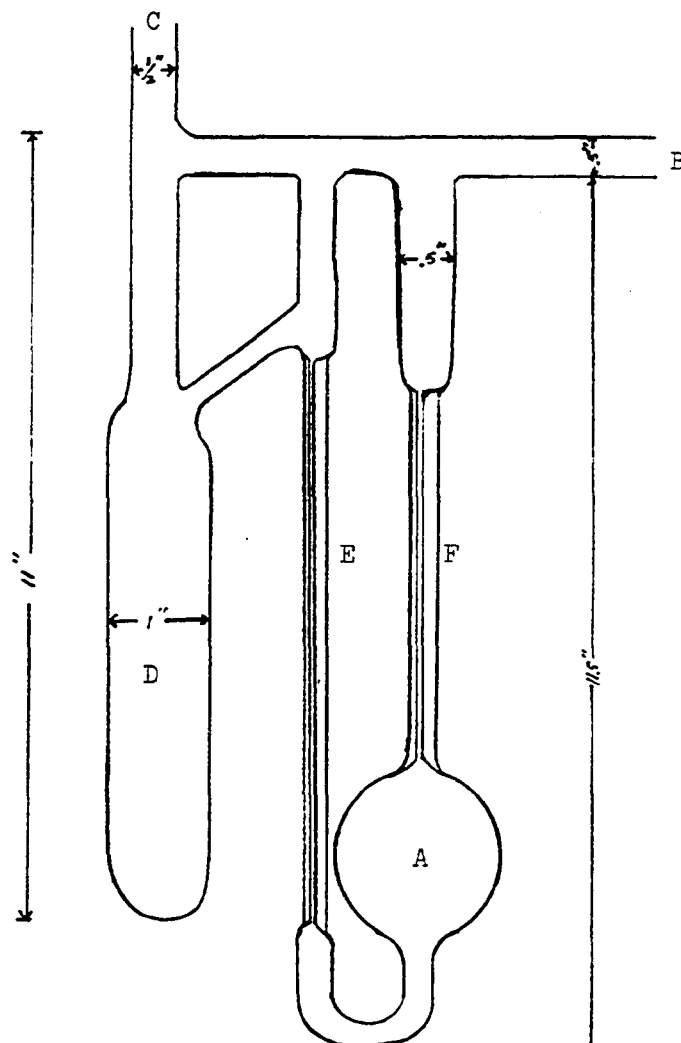


Figure 3. Dilatometer

during the calibration was within $\pm .005$ °C. (A calorimetric thermometer with uncertainty of $\pm .005$ °C from Parr Instrument Co. was used.) In this calibration, six temperatures and the corresponding height readings of the mercury in the capillaries were recorded. Then, the mercury was transferred to a container and weighed. From the weight and the densities of mercury at different temperatures (13), the average capillary radius and the reaction cell volume up to the base line were calculated: (See Table 2 for Data)

$$\bar{r} = \text{average radius} = 2.611 \times 10^{-2} \text{ cm.}$$

$$M = \text{mass of mercury} = 435.814 \text{ g.}$$

$$\begin{aligned} V_{\text{Hg},1} &= \text{volume of mercury at } 24.970 \text{ °C} \\ &= D_{24.970}^{-1} \times M = 32.2034 \text{ ml.} \end{aligned}$$

$$\begin{aligned} V_m &= \text{volume of reaction cell A, of} \\ &\quad \text{dilatometer to the marked line} \\ &\quad \text{on the capillary E =} \end{aligned}$$

$$V_{\text{Hg},1} + 2\pi\bar{r}^2 \Delta h = 32.243 \text{ ml.}$$

where Δh is the difference between the height reading of the marked line and the height reading corresponding to $V_{\text{Hg},1}$. In this case, $h_{\text{Hg},1} = 10.908 \text{ cm.}$, $h_m = 19.713 \text{ cm.}$, r_i = radius determined at different temperature = $(1/2\pi)^{1/2} \{ \Delta(M/D_i) / \Delta h_i \}^{1/2}$.

D. Determination of Purity of Di-tert-butyl Peroxide(11)

1. Reagents: All chemicals used were reagent grade unless otherwise specified. These reagents are glacial acetic acid, NaI (granular), 37% hydrochloric acid, standardized .101 N sodium thiosulfate (see Ref. 14), and iodine.

Table 2

Data from dilatometer calibration

t °C	D^{-1}	h_i^a	Δh_i^b	r_i^c
corrected	(ml./g.)	(cm.)	(cm.)	($\times 10^2$ cm.)
24.970	.0738897	10.408	----	----
25.150	.0739014	11.746	1.338	2.646
26.979	.0739148	13.076	1.330	2.656
27.978	.0739282	14.408	1.362	2.617
29.011	.0739412	15.848	1.410	2.588
29.979	.0739549	17.194	1.344	2.577

a. h_i : cathetometer reading

b. Δh_i : difference in cathetometer between two adjacent temperatures

c. r_i : average inner radius of two capillaries

2. Apparatus: The set-up consists of a reflux condenser, a three-neck, round bottom flask, a heating mantle, and a nitrogen supply.

3. Procedure: 50 ml. of glacial acid was put in the three-neck, round-bottom flask and refluxed briefly. The flow of nitrogen gas was carefully controlled. This process was performed in a hood to protect the reactants from bright sunlight. After the acid solution was refluxed 30 minutes, it was cooled and 6.0 g. sodium iodide was added. A sample of approximately 2.5 g. of peroxide and 2.0 ml. of 37% hydrochloric acid was then added to the solution. This mixture was heated to the boiling point of the mixture of glacial acetic acid, 37% HCl and di-tert-butyl peroxide immediately. The gas flow was cut off whenever the flask contents were boiled, and it was maintained slow at all other times to avoid undue loss of HI. After refluxing for an additional 50 minutes, 100 ml. of distilled water was added and the entire mixture was titrated with standardized .101 N sodium thiosulfate (14). A blank determination was also run, following the same procedures described above except for the addition of peroxide sample.

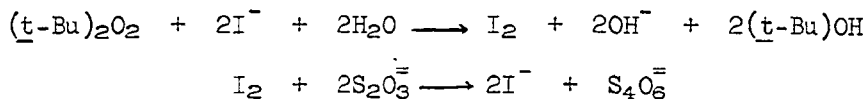
4. Calculations and Results: Data are listed in Table 3.

Table 3

Data from Determination of Purity of
Di-tert-butyl Peroxide

Vol. of Sodium Thiosulfate Used (ml.)	Blank (ml.)	Wt. of DTBP (ml.)	Purity %	Ave. %
41.35	.5	.354	85.0	87.4
46.85	.5	.381	89.8	

The reactions involved are:



The purity can be calculated in the following manner:

No. of milliequivalent of DTBP solution (assuming 100% purity)

$$= (\text{Wt. of DTBP sample} / \text{Equivalent wt. of DTBP}) \times 10^3$$

where equivalent weight of di-tert-butyl peroxide is 73.20 g./eq.

No. of milliequivalent of standardized .101 N

sodium thiosulfate (see Ref. 14)

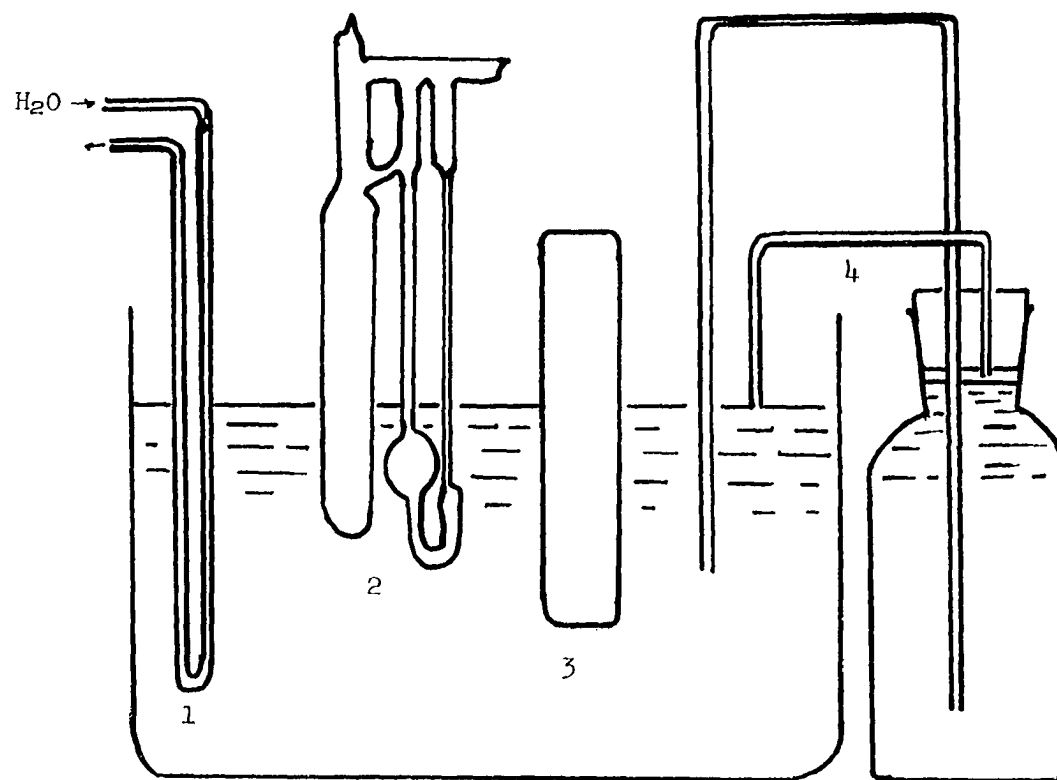
$$= \text{Normality} \times (\text{vol. of Na}_2\text{S}_2\text{O}_3 \text{ used})$$

So, purity of di-tert-butyl peroxide

$$= \frac{\text{No. of milliequivalent of Na}_2\text{S}_2\text{O}_3}{\text{No. of milliequivalent of DTBP solution}} \times 100\%$$

E. Determination of Rate of Polymerization

About 40 ml. of solution was prepared by mixing the purified α -methylstyrene and di-tert-butyl peroxide with a molar ratio of 100:1. The mixed solution was then transferred into a cleaned dilatometer with one end, C (see Figure 3), sealed off. The solution was degassed on a vacuum line by three cycles of freezing (with liquid nitrogen), evacuating, and thawing. This degassing process was done while the solution was in bulb D. Then the dilatometer was sealed off with a flame at B under vacuum and then was immersed in the thermostatic bath (see Figure 4) which had been adjusted to a desired temperature within $\pm .02^\circ\text{C}$. After temperature equilibration for about three hours, some of the solution was transferred from D to the reaction bulb A. This transfer brought the solution to a level below the marked line on capillary, E. The dilatometer was put in the bath again. In order to be sure that the temperature inside and outside the reaction bulb was uniform and a constant level reading could be obtained, the solution was left in the thermostatic bath overnight. Once a constant reading of the solution level was obtained, the solution was exposed to the UV light. The change in volume of the solution was followed by a cathetometer for a five-hour period. The volume change was plotted vs. time. The slope is proportional to the rate of conversion of monomer to polymer. A typical plot is shown in Figure 5 (for data, see Table 4).



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1. Cooling coil 2. Dilatometer 3. UV light source 4. Water level control system

Figure 4. Schematic representation for the set-up of free radical-initiated polymerization of α -methylstyrene

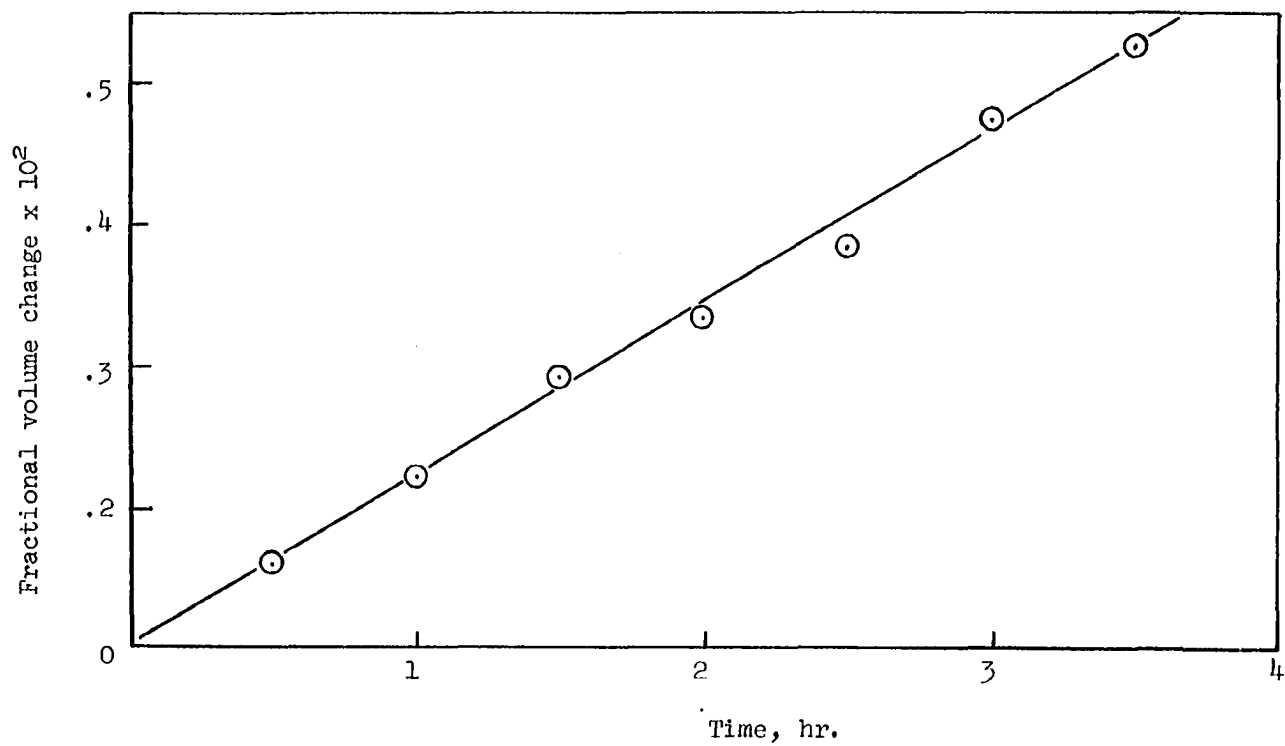


Figure 5. Rate of conversion of α -methylstyrene at 25 °C with .01 moles/mole monomer of di-tert-butyl peroxide as initiator

Table 4

Rate of conversion of α -methylstyrene
at 25 °C with .01 moles/mole monomer of di-tert-
butyl peroxide as initiator

<u>Time (hr.)</u>	<u>Fractional volume change $\times 10^2$</u>
.5	.160
1	.222
1.5	.283
2	.335
2.5	.384
3	.476
3.5	.526

After one trial at 25 °C, the solution in reaction bulb A was transferred back to cell D, and a thorough mixing was performed before another temperature trial. The same procedures were applied to other temperature trials with the same fill. The sequence of temperatures used was: 25, 30, 35, 40, 45, 50, 51, 55, 61, 64, 67, 70, 10, 15, 20 °C. The rate of conversion was plotted vs. temperature and the resulting curve is shown in Figure 6. The data are listed in Table 5.

The rate of conversion can be calculated from the following known quantities:

V_m = volume of reaction bulb, including capillaries
of the dilatometer to the marked line on the
capillary E

h_m = height reading of the marked line before reaction

h_I = average height reading of monomer solution
levels shown on capillaries before reaction

ΔV_i = difference in volume between h_m and h_I
 $= 2\pi \bar{r}^2 (h_m - h_I)$

where \bar{r} = the average inner radius of the capillaries.

$V_{init.}$ = initial volume of monomer solution
before reaction

ΔV_i = volume change of monomer solution per time interval
 $= 2\pi \bar{r}^2 (h_I - h_i)$

where h_i = an average height reading of solution levels shown on
capillaries after each time interval of reaction.

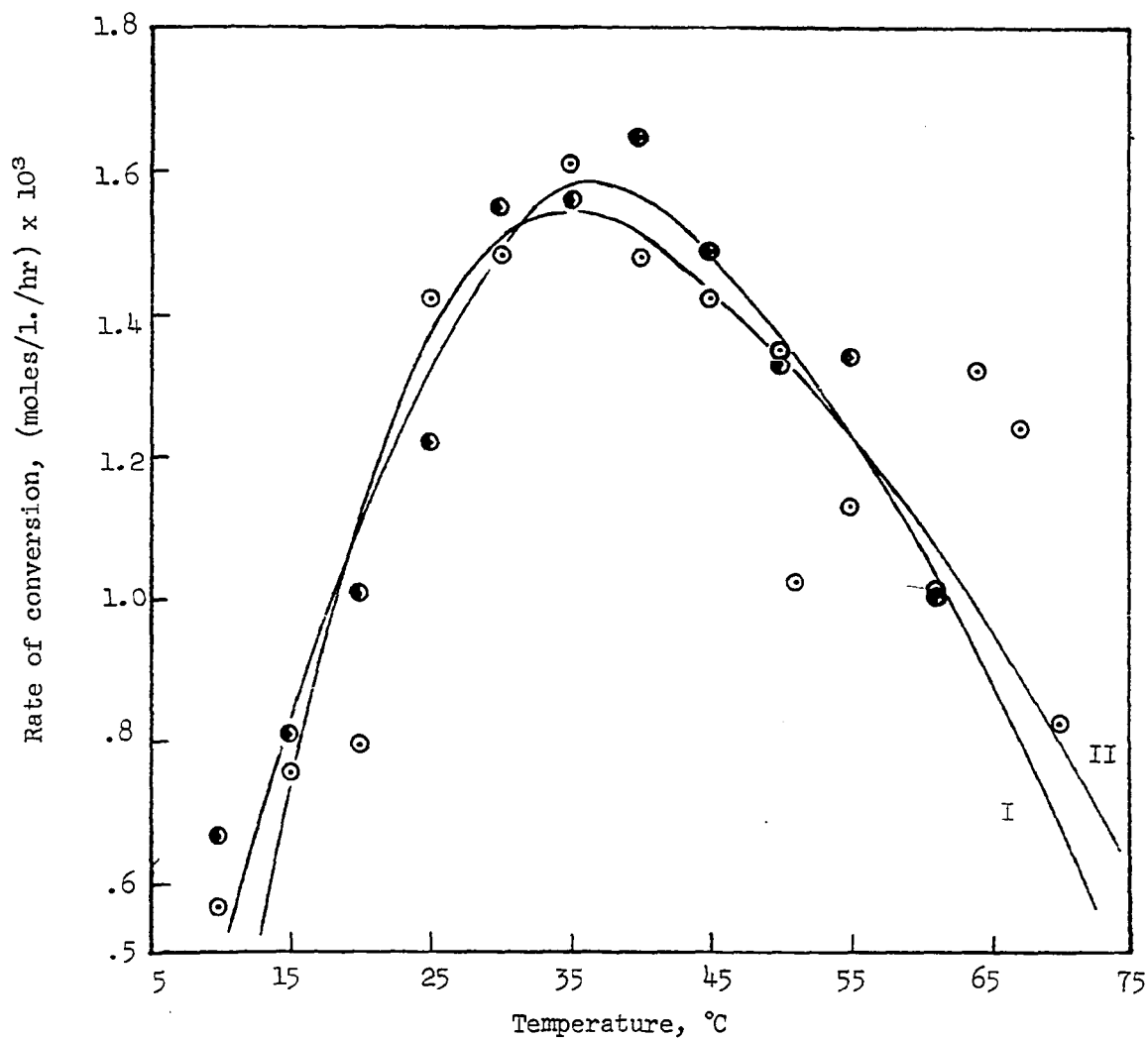


Figure 6. Rate of conversion of α -methylstyrene with .01 moles/mole monomer of di-tert-butyl peroxide as initiator from 10 to 70 $^{\circ}\text{C}$.

Note: Open circles for curve I (1st trial); half-shaded circles for curves II (2nd trial)

Table 5

Rate of conversion of α -methylstyrene with .01 moles/mole monomer of di-tert-butyl peroxide as initiator

t °C	R, (moles/l./hr.) $\times 10^3$		R ave.	R Normalized at 25 °C
	1st run	2nd run		
10	.570 ^a	.663	.616	.481
15	.754 ^a	.809	.782	.611
20	.794 ^a	1.07	.932	.728
25	1.43	1.22	1.28 ^b	1.00
30	1.48	1.55	1.52	1.19
35	1.61	1.56	1.58	1.23
40	1.48	1.65	1.56	1.22
45	1.42	1.49	1.46	1.14
50	1.35	1.33	1.34	1.05
51	.924	----	.924 ^c	.722
55	1.13	1.34	1.24	.969
61	1.06	1.04	1.05	.820
64	1.32	----	1.32 ^c	1.03
67	1.24 ^a	----	1.24 ^c	.969
70	.826	----	.826 ^c	.645

a. Average value from two successive runs

b. Average value obtained by four runs, two from the rate of initiation study

c. Value from a single run

The fractional volume change can be expressed as $\Delta V_i/V_{init.}$. The rate of conversion can be obtained by using dilatometric constant and monomer concentration, (APPENDIX A and B).

F. Determination of Rate of Initiation

The procedures of this method were the same as in the determination of the rates of polymerization described in the previous section. However, in this investigation, .0054 g. of purified benzoquinone, sealed into a tube under vacuum, was also put into the dilatometer before it was sealed off. The rate of polymerization was measured at 25 °C. Then the polymerizing solution was transferred back to the bulb D, and the inhibitor-filled tube was broken by shaking. After the polymerizing solution and the inhibitor were mixed well, the rate of polymerization in the presence of inhibitor was followed in the same way as in the determination of rate of polymerization.

The rate of initiation, R_i , can be calculated by $R_i = -ndQ/dt$ where "n" is the number of growing polymer radicals which react with one molecule of inhibitor; Q is the concentration of inhibitor added to the polymerizing solution, and "t" is the inhibition period. The data are listed in Table 6 (see Figure 7).

Table 6

Data from rate of initiation determination

Run	Code	$\overset{Q}{\text{(moles/l.)} \times 10^3}$	$\overset{R}{\text{(moles/l./hr.)} \times 10^3}$	$\overset{t}{\text{(min.)}}$	$\overset{\Delta}{R_i} \times 10^4$
1	A	.00	1.10	--	9.60
	B	1.20	.340	75	
2	C	.00	1.13	--	8.67
	D	1.20	.308	83	

Δ Assuming $n = 1$ and disregarding the retardation effect appeared;
unit: (moles/l./hr.)

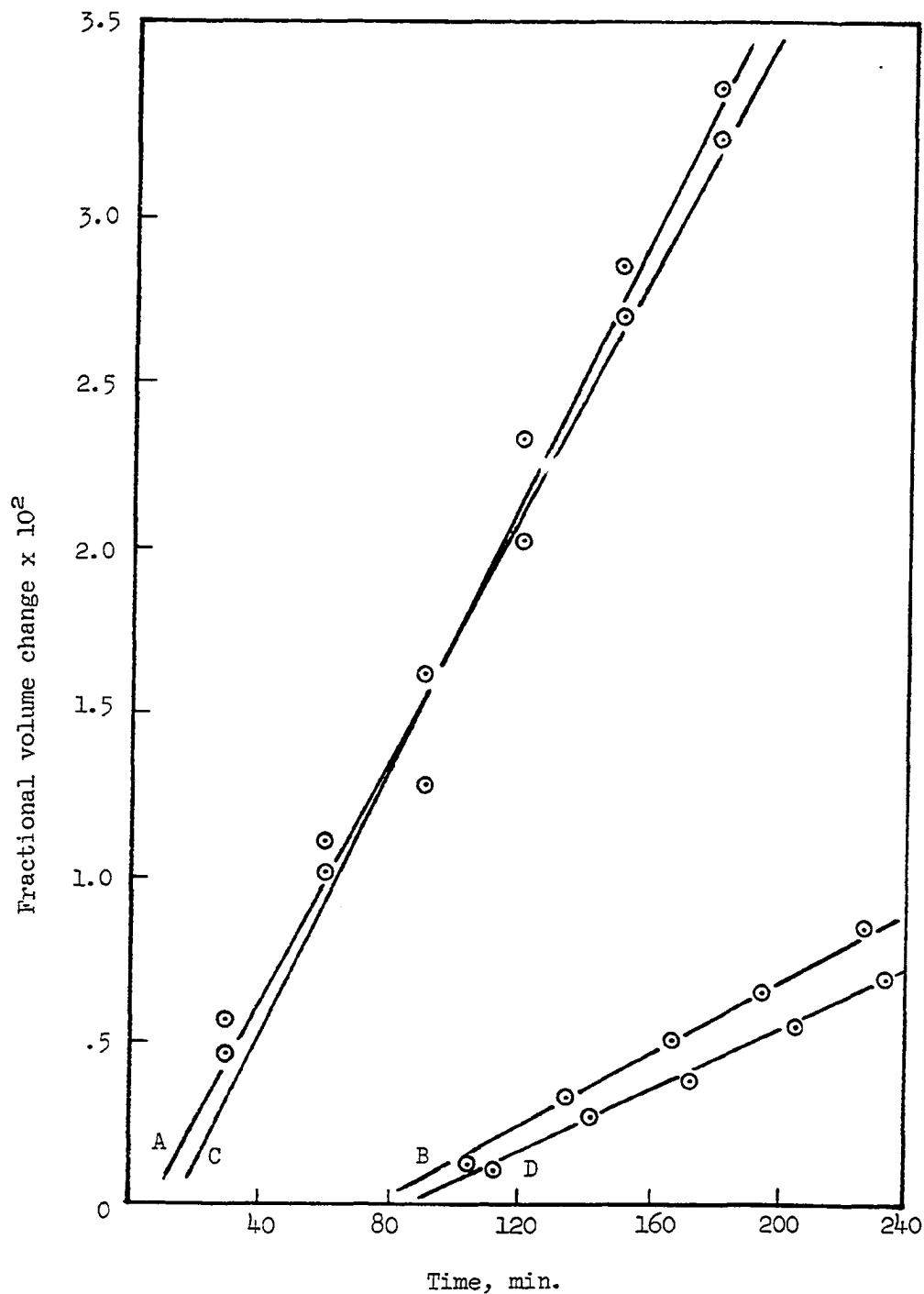


Figure 7. Rate of conversion at 25 °C (Curves A, C show the rate of conversion with .01 moles/mole monomer of di-tert butyl peroxide. Curves B, D show the rate of conversion using the same amount of initiator and 1.2×10^{-3} moles per liter of benzoquinone).

III. RESULTS AND DISCUSSION

A. Rate of Polymerization of α -Methylstyrene

The rate of polymerization of α -methylstyrene was studied over a temperature range from 10 to 70 °C. Reasonably straight lines were obtained by plotting the fractional volume change, $\Delta V_i/V_{init.}$, vs. time. A typical plot of these kinetic data at 25 °C is illustrated in Figure 5 and Table 4. The rate of polymerization which is proportional to the slope of the $\Delta V_i/V_{init.}$ - time plot of α -methylstyrene obtained at various temperatures are shown in Figure 6 and Table 5. When average values of rate of polymerization for two runs at each temperature were plotted against temperature, a curve was obtained as shown in Figure 8. It was found that the general shape of a plot of the rate of polymerization against temperature is in agreement with that suggested by Dainton and Ivin (see Figure 1). Extrapolation of the curve of rate of polymerization to higher temperatures, however, leads to an apparent ceiling temperature of about 80 °C. This result is not consistent with the reported value (4). The disagreement could be attributed to the different approaches followed. McCormick (4) who used the sodium-naphthalene catalyst in the polymerization of tetrahydrofuran determined the ceiling temperature to be 61 °C and demonstrated the linear relationship between the logarithm of the equilibrium concentration of monomer and the reciprocal temperature. However, no direct kinetic measurement of the rate of polymerization

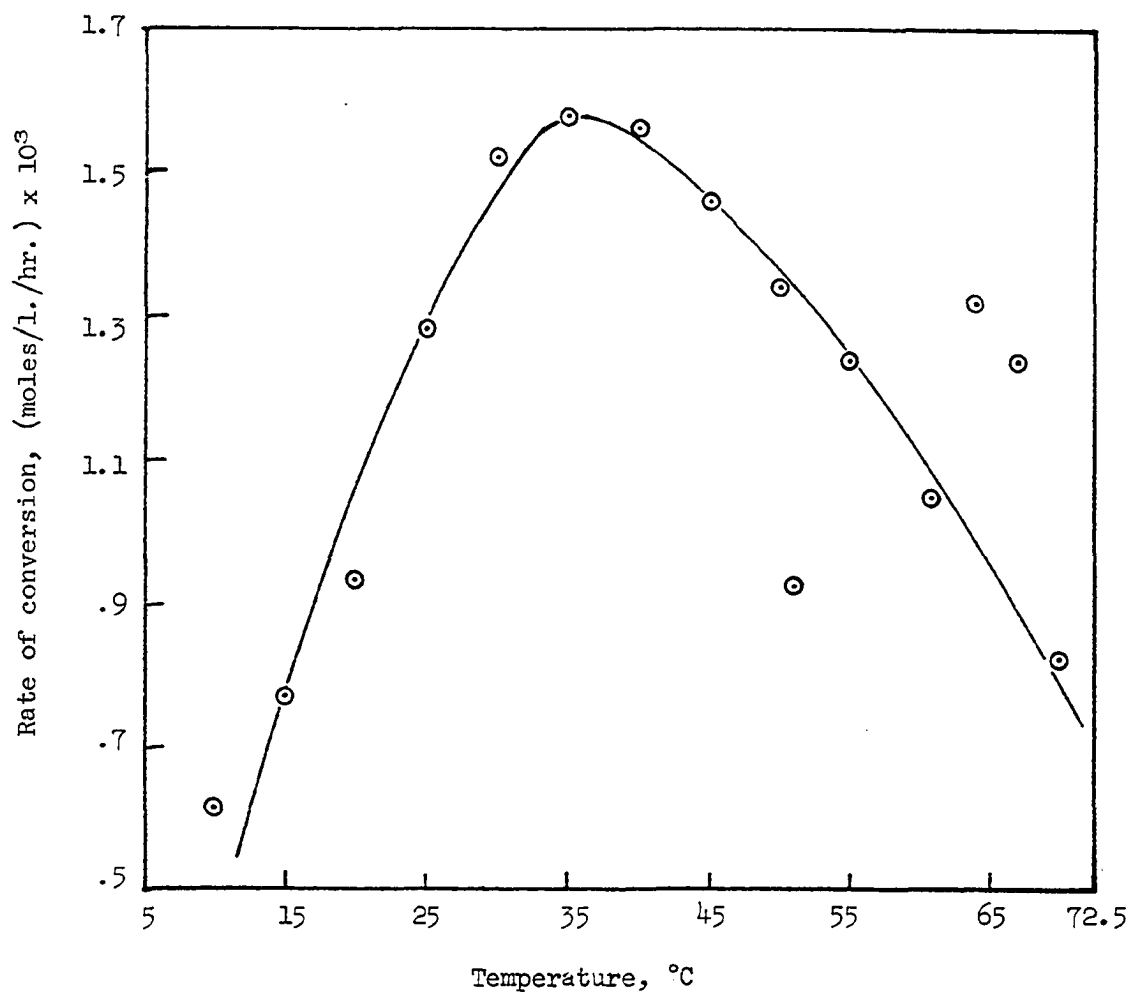


Figure 8. Rate of conversion of α -methylstyrene with .01 moles/mole monomer of di-*tert*-butyl peroxide (Average values of rate of conversion of two trials are used).

was shown. It is also worth mentioning that the highest temperature tried in McCormick's work is 60 °C. In this study, however, studies have been made up to 70 °C. Kilroe and Weale (15) have shown in their pressure-ceiling temperature relation studies of α -methylstyrene that the molecular weight of poly(α -methylstyrene) decreases as the temperature approaches the ceiling temperature ($T_c = 143$ °C at 4860 atm.). They also indicated that a large yield of dimer was obtained above the ceiling temperature. Dainton and Ivin (8) suggested that the depropagation was important in the region of ceiling temperature, but Bywater and Worsfold (16) pointed out that the depropagation is not significant for the short chain polymer formation. There is evidence that the heat of polymerization of short polymer chains (low molecular weight) is greater than that of longer polymer chains (higher molecular weight) (17). This information suggests that a higher apparent ceiling temperature is caused by dimerization reaction above the ceiling temperature 61 °C. In addition to this, the effect of $[R_1]$ in equation (6') which reduces the depropagation rate would also increase the apparent ceiling temperature. It can be seen that the general shape of the curve of rate of polymerization is skewed to the right compared to the theoretically predicted one.

B. Rate of Initiation

Generally there are three ways to determine the rate of initiation, namely, a) from the rate and degree of polymerization measurements, b) from initiator fragment analysis of polymers, and

c) from measurements of the rate of consumption of free radical scavengers added to the polymerizing system. Method "c" was used in this study. The results are shown in Table 6 and Figure 7. It can be seen from the rate of polymerization in the presence of benzoquinone that both inhibition and retardation effects are observed. For R_i determination, the rate of polymerization after the inhibition period should be the same as the rate of polymerization in the absence of inhibitor. Another problem encountered was the uncertainty regarding the number of growing polymer radicals which would react with one molecule of benzoquinone, i.e., "n" value in $R_i = -ndQ/dt$. Funt and Williams (18) have shown that the number of benzoquinone fragments in styrene increases to a limiting value with increasing benzoquinone concentration. However, the rate of increase must be different from monomer to monomer. The possibility that the copolymerization between benzoquinone and the monomer might occur to some extent, such as shown in the copolymerization of vinyl acetate with styrene (19) makes the system more complicated. It has been reported that ferric chloride (20) and cupric chloride (21) act as inhibitors, and both give a definite stoichiometric relationship in reacting with initiator radicals.

In order to obtain more satisfactory results in R_i determination, a further investigation is recommended. If we assume $n = 1$ and use the inhibition time observed, R_i can be tentatively calculated (see Table 6).

C. Reaction Rate Constants

If the rate of polymerization is normalized at 25 °C, $k_p/\sqrt{2k_t}$ can be calculated from eq. 7 by assuming $\alpha = 0$, $T_c = 61$ °C, and $\Delta H_p^\circ = -8$ kcal./mole. The calculated value for $k_p/\sqrt{k_t}$ is 2.36×10^{-4} l.^{1/2} mole^{-1/2} sec.^{-1/2}. Compared to the values of rate constants for styrene, i.e., $k_p/\sqrt{k_t} = 1.27 \times 10^{-1}$ l.^{1/2} mole^{-1/2} sec.^{-1/2}, this value is relatively small. This shows that α -methylstyrene is less easily polymerized by the free radical process.

D. Rate of Polymerization Obtained by Unsealed Dilatometer

Before using the dilatometer sealed off under vacuum, we tried numerous runs by using the unsealed dilatometer. The procedures followed were the same as those described before except that the polymerizing solution had not been degassed by the freezing, thawing and evacuating cycles but was exposed to the atmosphere. One set of data obtained is shown in Figure 9 and Table 7. It can be seen that the rates of polymerization are comparatively lower than those shown in Figure 6. This could be explained in terms of the presence of oxygen which is known to be a retarder in polymerization. A rather surprising phenomenon was observed for the rate of polymerization above 50 °C which shows a non-decreasing rate with an increase in temperature. It is surmised that the decreasing solubility of oxygen with the increase in temperature might reduce the retardation effect. Some other unknown erratic cause might also

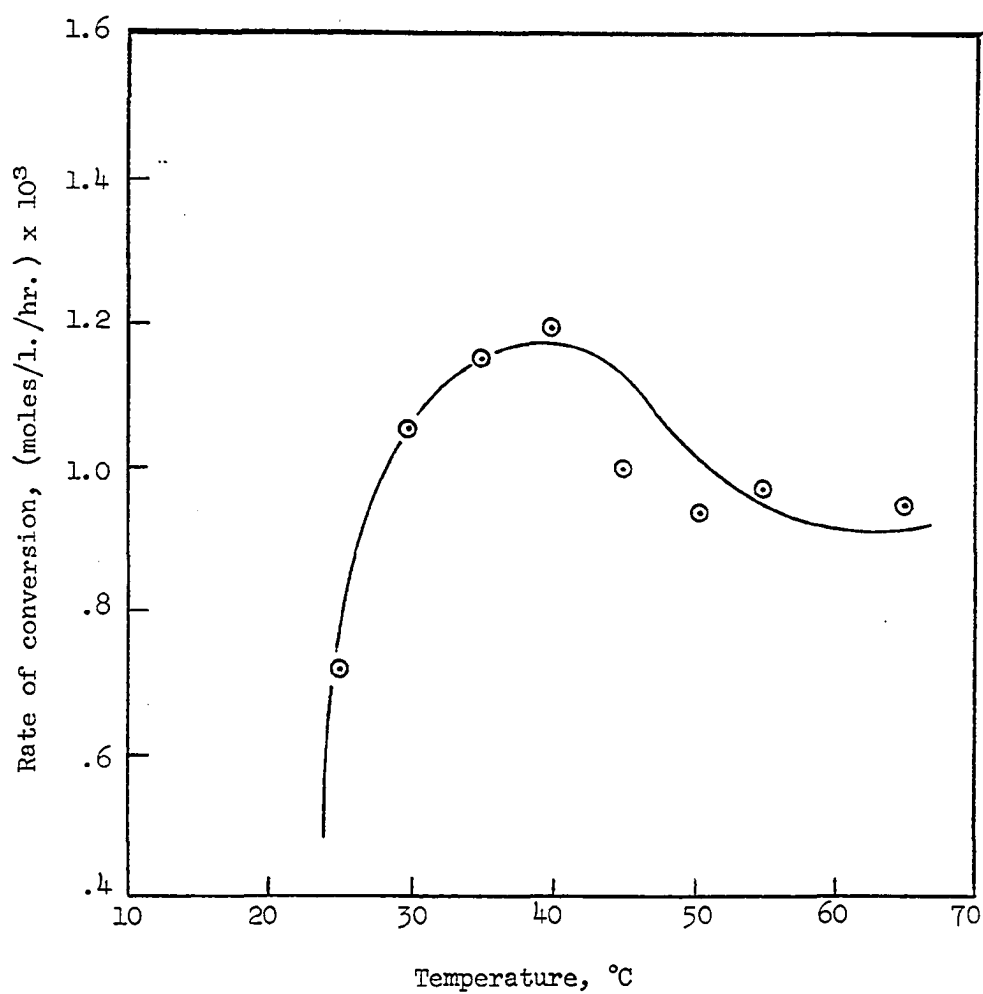


Figure 9. Rate of conversion of α -methylstyrene with .01 moles/mole monomer of di-tert-butyl peroxide as initiator using an unsealed dilatometer

Table 7

Rate of conversion of α -methylstyrene
with .01 moles per mole monomer of di-
tert-butyl peroxide as initiator using
an unsealed dilatometer

<u>t °C</u>	<u>$\frac{R}{(\text{moles/l. /hr.}) \times 10^3}$</u>
25	.717
30	1.05
35	1.10
40	1.19
45	.942
51	.936
55	.970
65	.945

be involved. There is no doubt that atmospheric oxygen has a very marked effect on the polymerization of α -methylstyrene.

E. Thermal Effect of UV Light Irradiation

Before observing the volume change of solution on polymerization, the dilatometer was set in the thermostat until a constant reading of the level of solution in the capillary (e.g. h_I) was obtained. Once the UV light source was turned on, the level of solution rose apparently because of a thermal effect of the light source. After a period of time, the level dropped back to the original value, when the expansion was compensated by the contraction effect of polymerization. This effect is illustrated in Figure 10.

The apparent temperature rise on irradiation can be calculated from the apparent expansion of solution. Data are listed in Table 8.

The apparent temperature rise of the polymerizing solution in the reaction cell on irradiation can be calculated as follows:

$$\text{Density at } t_1 \text{ } ^\circ\text{C: } \rho_{t_1} = \text{wt.}/V_{t_1}$$

$$\text{Similarly, at } t_2 \text{ } ^\circ\text{C: } \rho_{t_2} = \text{wt.}/V_{t_2}$$

$$\text{Since } \rho_{t_1} \cdot V_{t_1} = \rho_{t_2} \cdot V_{t_2}$$

$$\text{So } \rho_{t_1} [V_m - 2\pi \bar{r}^2(h_m - h_I)] = \rho_{t_2} [V_m - 2\pi \bar{r}^2(h_m - h_I - h_{irr})] \quad (8)$$

$$\text{Where } h_{irr} = h_{max} + h_{poly} \text{ (see Figure 10)}$$

$$\text{At } t_1 = 24.99 \text{ } ^\circ\text{C, } \rho_{t_1} = .928303 - 8.86486 \times 10^{-4}t_1 - 1.61072 \times 10^{-9}t_1^2$$

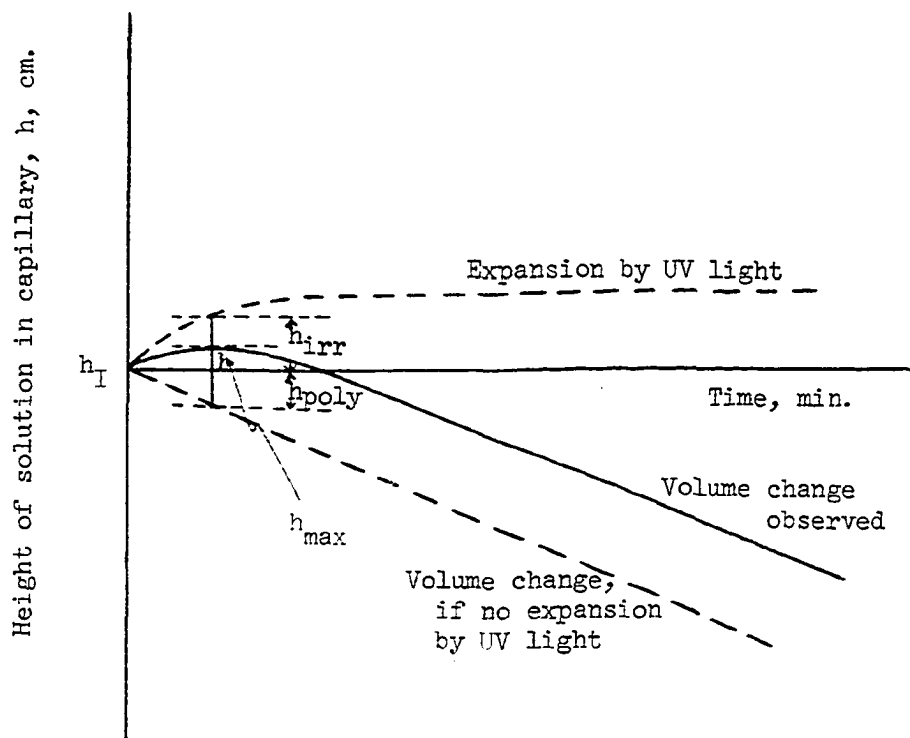


Figure 10. Thermal expansion by UV light on polymerization of α -methylstyrene

Table 8

Data from thermal expansion
of polymerization solution on irradiation

<u>t °C</u>	Thermal expansion (cm.)	
	<u>1st run</u>	<u>2nd run</u>
25	.074	.066
30	.127	.058
40	.075	.071
61	.085	.062

From data (see Table 8), the expansion on irradiation, h_{irr} , is calculated $.700 \times 10^{-1}$ cm.

$$V_m = 32.2432 \text{ ml.}$$

$$h_m = 19.468 \text{ cm.}$$

$$h_I = 11.604 \text{ cm.}$$

If $P_{t_2} = .928303 - 8.86486 \times 10^{-4}t_2 - 1.61072 \times 10^{-9}t_2^2$, then t_2 can be solved from eq. 8. The value solved for t_2 is 25.00°C , i.e. the temperature rise is $.01^\circ\text{C}$. This value is small compared to the temperature uncertainty. However, the effect on the monomer solution expansion is noticeable. The temperature control is critical, especially in the region of ceiling temperature.

IV. SUMMARY AND CONCLUSION

1. Rate of polymerization of α -methylstyrene was studied dilatometrically at temperatures from 10 to 70 °C by free radical-initiated mechanism.

2. Atmospheric oxygen had a marked effect on polymerization of α -methylstyrene and gave inconsistent results in rate of polymerization.

3. Rate of polymerization of α -methylstyrene studied in the absence of oxygen increases and then decreases as temperature increases. A maximum rate at about 40 °C was observed. The general shape of this curve is as expected from previously reported theories.

4. An appreciable rate of polymerization of α -methylstyrene was observed even above the ceiling temperature of 61 °C, probably because of an effect of molecular weight on ceiling temperature and a significant fraction of radicals that cannot depropagate in the region of ceiling temperature.

5. Benzoquinone showed both inhibition and retardation effects in the determination of rate of initiation. A more extensive study of inhibition is recommended.

V. APPENDIX

A. Density and Concentration of Monomer (22)

Based on the Dow Chemical Company Bulletin: "Styrene Type Monomers", the following two equations were obtained by least squares fit (double precision) on the PDP-10 computer. Values of density and concentration of α -methylstyrene monomer at various temperatures agree with reported values within experimental error over a range from 0 to 160 °C (no values were available outside this range for testing).

Density of α -methylstyrene at t °C, g./cm.³:

$$\rho_t = .928303 - 8.86486 \times 10^{-4}t - 1.61072 \times 10^{-9}t^2$$

Concentration of pure α -methylstyrene, moles/l.:

$$[M]_t = 7.85568 - 7.50385 \times 10^{-3}t - 5.510158 \times 10^{-10}t^2$$

B. Dilatometric Constant (23)

For α -methylstyrene, we use a dilatometric constant of $c_D^{25} = \Delta V_i/V_{init.} = .187$ at 25 °C for 100% conversion of monomer to polymer. Then, to obtain the dilatometric constant at any other temperature, it was assumed that there is essentially no coefficient of thermal expansion for the polymer, and

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

where ρ_t is the same as in APPENDIX A. Combining this with $[M]_t$, for monomer concentration as a function of t °C, conversion of monomer to polymer in moles per liter corresponding to a given fractional

volume change can be calculated:

Conversion in moles per liter

$$= [M]_t \times \frac{\Delta V_i/V_{init.}}{C_D^t}$$

where $\Delta V_i/V_{init.}$ is the fractional volume change of monomer solution.

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