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# The Thermal Polymerization of Methyl Methacrylate

BY CHEVES WALLING AND EMORENE R. BRIGGS

Up to the present, kinetic investigations of thermal polymerization to high molecular weight products have been almost entirely restricted to styrene, for the sound reason that it is the only monomer with which different investigators have obtained reproducible results.[1] Although Starkweather and Taylor[2] reported an initial rate of polymerization of vinyl acetate of 30% per hour at 100°, Cuthbertson, Gee and Rideal[3] and Breitenbach and Raff[4] found that, with suitable precautions, the monomer was stable for days at this temperature. The latter workers also obtained similar results with methyl acrylate.[4] Similarly, Flory has reported rate studies on methyl methacrylate as giving unreproducible rates and probably representing a catalytic reaction.[5] This paper describes a new investigation of the thermal polymerization of methyl methacrylate, using rather elaborate precautions to eliminate trace catalysis or inhibition, which had led us to the conclusion that in the temperature range 100–150°, methyl methacrylate does undergo a reproducible thermal polymerization. At 131° the reaction has a rate of 0.125% per hour, approximately one-hundredth that of styrene.

**Establishment of a Reproducible Rate of Polymerization.**—Preliminary experiments at 60 and 100° using ordinary vacuum technique in putting up reaction tubes gave rates of polymerization of methyl methacrylate which were not reproducible. As the most likely reason for the erratic results appeared to be the inadvertent introduction of traces of catalyst, presumably oxygen or peroxides, an apparatus was designed which made it possible to store the methyl methacrylate, measure it, and finally introduce it into reaction tubes without exposure to air and with the minimum exposure to light. Next, the reaction temperature was raised to 131° and an antioxidant sought which would suppress the formation of peroxides from any traces of oxygen which might be present, or destroy any which might have been formed. The observation, originally made by Breitenbach, Springer and Horeischy[6] that hydroquinone in the absence of air has no effect on the rate of thermal polymerization of styrene, made hydroquinone appear a likely choice, particularly when it was found that it had no inhibiting effect upon the photochemical polymerization at room temperature. Thus a sample of methyl methacrylate sealed under vacuum in a Pyrex tube and exposed to a carbon arc gave 9% polymer in six hours, while a similar tube containing 2.5% hydroquinone gave 16.4% polymer under identical conditions. The increase in rate is presumably due to light absorption and photosensitization in the near ultraviolet by the hydroquinone.[7]

When polymerizations were carried out at 131° in tubes put up with the improved apparatus in the presence of 0.01 or 0.1 weight per cent. of hydroquinone, reproducible results were obtained as shown in Fig. 1. Larger quantities led to a slight drop in rate.

That the consistent rates of Fig. 1 were not due to a reaction specifically catalyzed by hydroquinone is shown in Fig. 2, which illustrates rates observed in the presence of 0.1 weight per cent. of

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(1) For discussion and references, see Walling, Briggs and Mayo, THIS JOURNAL, **68**, 1145 (1946).

(2) Starkweather and Taylor, *ibid.*, **52**, 4708 (1930).

(3) Cuthbertson, Gee and Rideal, *Nature*, **140**, 889 (1937).

(4) Breitenbach and Raff, *Ber.*, **69**, 1107 (1936).

(5) Flory, THIS JOURNAL, **59**, 241 (1937).

(6) Breitenbach, Springer and Horeischy, *Ber.*, **71**, 1438 (1938).

(7) The common use of the term "inhibitor" for phenolic materials is confusing, for in moderate quantities and in absence of air they have little effect on rates of thermal polymerization. In the presence of air or peroxides, however, they do retard polymerization, presumably by destroying or preventing the formation of peroxides, *cf.* Walling, THIS JOURNAL, **66**, 1602 (1944), or by the formation of *bona fide* inhibitors such as quinones.[6] A better term would be "antioxidants" or "anticatalysts," reserving the term "inhibitor" for materials which actually stop the growing polymer chains.

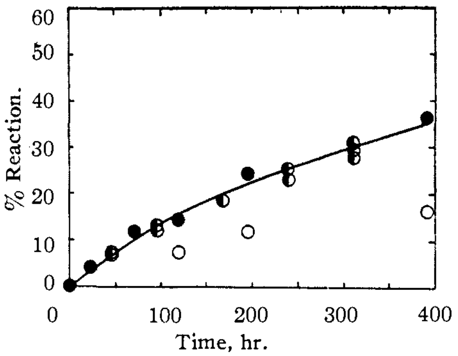

Fig. 1.—Thermal polymerization of methyl methacrylate at 131° in the presence of hydroquinone: ● 0.01 wt. %.; ◐ 0.1 wt. %; ○ 1.0 wt. %.

*t*-butylcatechol and pyrogallol. In fact, it was later found that similar rates were also obtained in the absence of any antioxidant whatsoever, providing the monomer was never exposed to light brighter than a red photographic safe light from the time it was distilled into the reaction tubes. Rates for some experiments put up in this way are also included in Fig. 2.

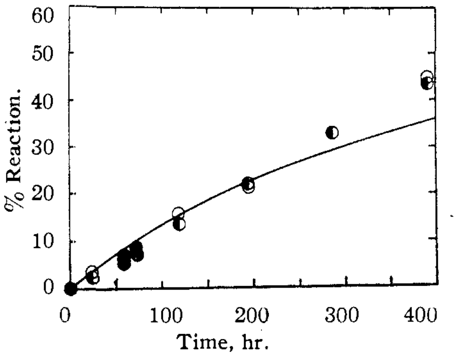

Fig. 2.—Thermal polymerization of methyl methacrylate at 131° in the presence of: ○ 0.1% *t*-butylcatechol; ◐ 0.1% pyrogallol; ● no antioxidant. Solid line is rate curve in the presence of hydroquinone from Fig. 1.

Although the apparatus employed to measure and handle the methyl methacrylate appeared to be highly successful in eliminating traces of catalyst, the presence of mercury actuated valves inevitably introduced traces of mercury vapor into the system. In order to determine whether mercury had any effect upon polymerization rate, a series of experiments were put up in which the monomer was distilled through a trap containing a sodium mirror.[8] As shown in Fig. 3, identical polymerization rates were observed in presence and absence of the sodium trap, so it may be concluded that traces of mercury have no effect upon the polymerization rate.[9]

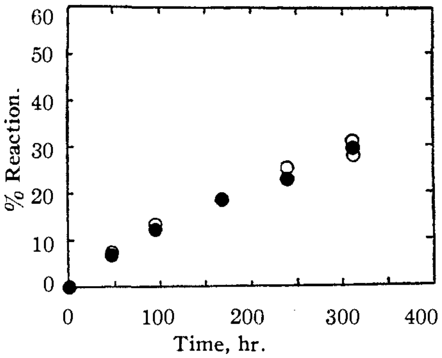

Fig. 3.—Effect of mercury vapor on the rate of thermal polymerization of methyl methacrylate at 131°; ● experiments using sodium trap; ○ experiments not using trap.

Our success in attaining a reproducible rate of polymerization at 131° led us to try experiments at other temperatures. Figure 4 illustrates results obtained at 150° and Table I results at 100°, both in the presence of 0.1 weight per cent. hydroquinone.

TABLE I

THERMAL POLYMERIZATION OF METHYL METHACRYLATE AT 100°

| Time, hr. | Reaction, % | %/hr. |
|---|---|---|
| 168 | 4.90 | 0.029 |
| 168 | 4.64 | .028 |
| 168 | 3.66 | .022 |
| 336 | 6.85 | .020 |
| 336 | 6.85 | .020 |
| | | Av. .024 |

Although good reproducibility was obtained at 150°, at 100° some spread in rates occurred, and it appears likely that we are approaching the point where, due to the extreme slowness of the thermal reaction, our technique is no longer able to suppress all trace catalysis or inhibition.

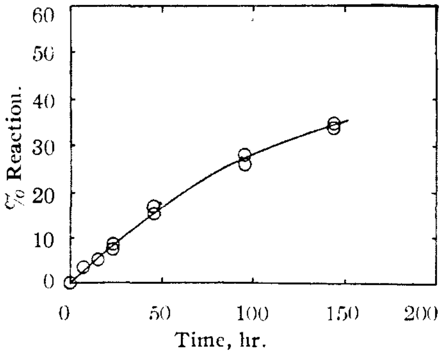

Fig. 4.—Thermal polymerization of methyl methacrylate at 150° in the presence of 0.1% hydroquinone.

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[8] This technique is reported to be as effective in removing mercury vapor as a trap cooled in liquid nitrogen, *cf.* Hughes and Poindexter, *Nature*, **15**, 979 (1925). Qualitatively, it was successful in that the methacrylate condensed in the reaction tube was snow-white instead of grayish due to traces of finely divided mercury as occurred when no trap was used.

[9] A similar conclusion has been arrived at for the photochemical reaction, Melville, *Proc. Roy. Soc.* (London), **163A**, 511 (1937).

**Discussion of Kinetic Results.**—The reproducibility of rates under what were intended to be critical variations in experimental conditions seems to leave little doubt that, in the experiments described in the preceding section, we have been dealing with a *bona fide* thermal polymerization similar to that of styrene. The best initial over-all rates for the polymerization (in moles per liter per sec.) at 100, 131 and 150°, taken from the data of Figs. 1–4 and Table I, are given in Table II. From these rates the over-all activation energy has been determined in the usual manner as 16,000 ± 2,000 cal./mole, appreciably lower than that observed for the more rapid polymerization of styrene.

TABLE II

INITIAL RATES OF MONOMER DISAPPEARANCE AND RATE CONSTANTS IN THE THERMAL POLYMERIZATION OF METHYL METHACRYLATE

| Temperature, °C. | 100 | 131 | 150 |
|---|---|---|---|
| Rate × $10^6$ (moles/liter/sec.) | 0.624 | 3.25 | 8.32 |
| $k_b/k_c \times 10^2$ | 7.30 | 21.1 | 37.1 |
| $k_a \times 10^{15}$ | 0.698 | 6.54 | 24.4 |
| Kinetic chain length × $10^{-6}$ | 5.1 | 2.8 | 1.9 |

Schulz and Blaschke[10] have recently reported an extensive study of the benzoyl peroxide catalyzed polymerization of methyl methacrylate. Using a complicated scheme of chain initiation which is consistent with the experimental data,[11] and assuming the usual bimolecular chain growth and chain termination, they find $k_b^2/k_c$ 2.19 × $10^{-2}$ at 70° and $2E_b - E_c = 10{,}300$ cal./mole, where $k_b$, and $E_b$, $k_c$ and $E_c$ are rate constants and activation energies for chain growth and chain termination, respectively, and all quantities are measured in moles, liters and seconds.

If the usual scheme of bimolecular initiation, growth and termination which has been applied to the thermal polymerization of styrene[1] may also be applied to methyl methacrylate, the over-all rate expression becomes $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_b\sqrt{k_a/k_c}[\mathrm{M}]^2$ where [M] is concentration of monomer, $k_a$ the rate constant for thermal chain initiation, and $k_b$ and $k_c$ the same rate constants measured by Schulz and Blaschke in the catalyzed reaction, since both catalyzed and thermal reactions are presumed to proceed through the same radical intermediates.[12] Since Schulz and Blaschke measured $2E_b - E_c$, it is possible to extrapolate their $k_b^2/k_c$ ratio to the temperatures at which the thermal reaction was studied, and, knowing [M] and $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t$, solve for $k_a$. Values are listed in Table II. Further, as the over-all activation energy for the reaction, 16 kcal., is equal to $1/2E_a + E_b - 1/2E_c$, $E_a = 22$ kcal. By the relation $v_a = A_a e^{-E_a/RT}$, the frequency factor for thermal initiation may be calculated as approximately 0.36. This value, which requires that only about one in $10^{12}$ collisions between methacrylate molecules having the requisite energy be effective in initiating polymerization, is even smaller than that reported for the thermal isomerization of *cis*-2-butene.[13]

A value of a frequency factor so far below that usually encountered is a surprise and, admittedly, is the result of a chain of reasoning which assumes: (1) an actual uncatalyzed reaction has been measured; (2) the mechanisms assumed are correct[14]; and (3) the data of Schulz and Blaschke are accurate. However, it appears less implausible when it is realized that a simple reaction having such characteristics would proceed at a rate of only about 0.1% per hour at 500° and could only rarely be observed experimentally. It is entirely possible that many such reactions exist, but that we can only expect to find them in a case like that occurring here, where their effect is magnified several millionfold through the initiation of a chain reaction. Since the frequency factor for chain initiation of styrene is of the order of $10^5$,[15] this difference in frequency factors, partly compensated for by a lower activation energy and longer kinetic chain-lengths for methacrylate, accounts for the great difference in rate of thermal polymerization of these monomers.

Knowing the rates of production of active centers and disappearance of monomer, it is possible to calculate the average kinetic chain length in methacrylate polymerization. Results (assuming each center, by its biradical nature, to give rise to two chains) will be found in Table II and indicate *kinetic chain lengths* of several million although, due to chain transfer, the actual *polymer molecules* are much smaller. This remarkably long chain length indicates why such care is necessary in studying methacrylate polymerization, as an inhibitor with which an active center reacts only once in every million growth-reactions, or a catalyst producing only $10^{-12}$ moles of active centers per second will have a pronounced effect on the polymerization rate. In contrast, styrene, with kinetic chain-lengths rarely exceeding $10^4$, would be expected to prove, as has been the case, a much more tractable monomer for kinetic studies.

**Degree of Polymerization.**—In Table III are listed intrinsic viscosities in chloroform, and degrees of polymerization, using the relationship determined by Schulz and Dinglinger[16] of sample polymerizations at different temperatures in the presence of various amounts of hydroquinone.

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(10) Schulz and Blaschke, *Z. physik. Chem.*, **B51**, 75 (1942).

(11) A more plausible interpretation of the same data has recently been proposed in a paper from this Laboratory, *cf.* Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(12) Since we are dealing here solely with initial rates of reaction the question of activities of activated complexes raised in reference (1) does not arise.

(13) Kistiakowsky and Smith, THIS JOURNAL, **58**, 766 (1936).

(14) It may be noted that other mechanisms involving only a change in the order of chain initiation will make only a minor change in $k_a$ and the frequency factor.

(15) Unpublished work carried out in this Laboratory by Dr. R. A. Gregg.

(16) Schulz and Dinglinger, *J. prakt. Chem.*, **158**, 136 (1941).

At 131° it will be seen that 0.1% hydroquinone has little effect on the degree of polymerization, and, from results in the presence of 1.0%, a transfer constant[17] of approximately 0.01 may be calculated. Schulz and Blaschke (using the same viscosity-degree of polymerization relation) have determined the transfer constant for the methyl methacrylate-type radical with methyl methacrylate as $6.8 \times 10^{-5}$ at 70°, the activation energy for transfer being 5650 cal./mole higher than for chain growth. Using these data, the highest possible degrees of polymerization with pure methyl methacrylate at 100, 131 and 150° may be calculated as 7600, 4200 and 3100, respectively. Our results will be seen to be appreciably higher.

TABLE III

AVERAGE DEGREE OF POLYMERIZATION ($\bar{P}$) FOR THERMALLY POLYMERIZED METHYL METHACRYLATE

| Temp., °C. | % Hydroquinone | $[\eta]$ | $\bar{P}$ |
|---|---|---|---|
| 100 | 0.1 | 6.27 | 10500 |
| 131 | .0 | 4.75 | 7900 |
| 131 | .0 | 4.36 | 7240 |
| 131 | .1 | 4.03 | 6680 |
| 131 | .1 | 4.57 | 7590 |
| 131 | 1.0 | 2.63 | 4300 |
| 131 | 1.0 | 2.88 | 4730 |
| 150 | 0.1 | 3.12 | 5130 |
| 150 | .1 | 3.17 | 5220 |
| 150 | .1 | 3.11 | 5120 |

## Experimental

**Polymerization Technique.**—In order to eliminate as far as possible the presence of air or other contaminants during polymerization, all handling of monomer and filling of reaction tubes was carried out in a special apparatus, illustrated in Fig. 5, attached to a high-vacuum line. To prepare the apparatus for use, it was first thoroughly flamed out under vacuum. A tube containing approximately 200 cc. of freshly distilled methyl methacrylate ($n^{20}_{\mathrm{D}}$ 1.4142–1.4148, boiling over a 0.1° range) was next attached at (A), frozen in dry ice, degassed twice and then distilled under high vacuum into (B) where it was stored until needed. (B) was wrapped in tin-foil to exclude light and, except when monomer was being distilled from it, kept in a Dewar flask filled with Dry Ice. Air was excluded by depressing the plungers of the 50-cc. Pyrex hypodermic syringes (E, F) forcing mercury up into the U-tubes and floating the glass valve-plungers (C) up against the valve seats (D) which they had been ground to fit. The hypodermic plungers could be locked in position by stirrups fitting over their tops and secured to the syringe barrels. The valve seats at (D) and the syringe barrels were both sufficiently tight to withstand an atmosphere pressure differential for weeks without leakage.

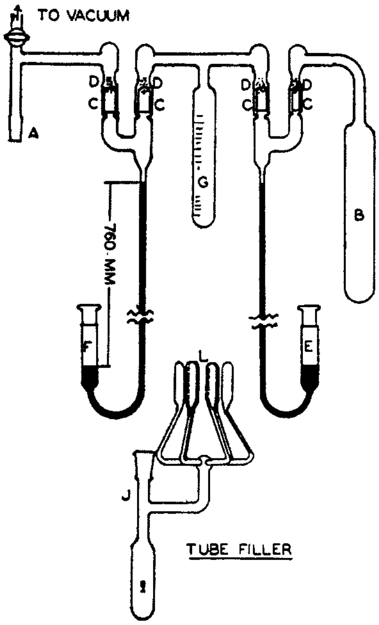

Fig. 5.—Apparatus for handling methyl methacrylate in the absence of air.

Polymerizations were usually carried out in small reaction-tubes (L) of approximately 5-cc. capacity, filled by means of the illustrated tube-filler. This filler was attached at (A), and monomer distilled into the measuring tube (G) made from a piece of graduated Pyrex buret. By suitable manipulation of valves, a measured amount of monomer was distilled into (I) (which contained a known amount of hydroquinone or other desired additive), given a dual precautionary degassing and frozen. The tube-filler was next sealed off at (J), removed from the apparatus, and (I) brought to room temperature. The reaction-tubes (L) were filled by suddenly inverting the tube-filler, plunging them into Dry Ice, and sealing each off. The tubes were then wrapped in tin-foil and placed in suitable thermostats for whatever time was desired. The extent of polymerization was followed by removing, cooling and opening tubes and determining the index of refraction of their contents. A number of experiments in larger tubes in which the polymer was worked up by the method of Lewis and Mayo[18] and determined gravimetrically established that, up to 40% reaction, 1% reaction corresponded to an increase in index of 0.00094.

Experiments in the absence of mercury vapor were made using a special tube-filler in which all vapors passed over a sodium mirror before being condensed at (I). Those in the dark were carried out by filling tubes at night with the minimum use of a red photographic safe-light to read volumes, etc.

**Viscosity measurements** were made on chloroform solutions of polymer having relative viscosities of 1.5–2.0. Intrinsic viscosities were calculated by the equation $\ln \eta_{\mathrm{rel}}/C = [\eta]$, and degrees of polymerization calculated by the relation determined by Schulz and Dinglinger for unfractionated polymer.[16]

**Acknowledgment.**—The authors wish to thank Dr. Frank R. Mayo for his interest and many helpful discussions during this investigation.

## Summary

1. By the use of suitable precautions, a reproducible polymerization of methyl methacrylate has been obtained between 100–150° in the absence of added catalysts. This is thought to represent a true thermally initiated reaction with an over-all activation energy of 16 kcal.

2. Combining the data reported here with those of Schulz and Blaschke, and assuming a mechanism of bimolecular initiation, growth and termination, the thermal initiation reaction has been calculated to have an activation energy of 22 kcal. but a frequency factor of less than unity.

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[17] Mayo, THIS JOURNAL, **65**, 2324 (1943).

[18] Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

The average kinetic chain length is approximately three million in this temperature range, but polymer molecules are much smaller due to chain transfer.

3. The transfer constant for the methacrylate radical with hydroquinone is approximately 0.01.

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# The Kinetics of the Thermal Polymerization of Styrene

BY CHEVES WALLING, EMORENE R. BRIGGS AND FRANK R. MAYO

In the past eight years the uncatalyzed, purely thermal polymerization of styrene has been studied by several workers in different laboratories.[1] Since, with reasonable precautions, reproducible and consistent rates have been obtained, the existence of such an uncatalyzed reaction appears to have been demonstrated with a good deal of certainty. Nevertheless, although most workers favor a mechanism of bimolecular initiation, growth, and termination,[2] the rates of the separate steps are subjects of conjecture. Furthermore, a very important anomaly exists: while it has been amply demonstrated that the initial rate of thermal polymerization is second order in respect to styrene in a number of solvents,[1a,1c,1e] the rate in pure styrene in the range 0–90% reaction is approximately first order.[1d] This change in order leads to the rather striking result that *a 10% solution of styrene in polystyrene polymerizes approximately ten times as rapidly as in other solvents.*

**Polymerization in Changing Medium.**—Any attempt to interpret such a change in kinetic order leads at once into the important, but obscure, problem of the effect of changing medium upon reaction rates. Customarily, the problem is treated by the Brønsted rate equation[3] which states that in the reaction A + B → C the reaction rate is given by $k[\mathrm{A}][\mathrm{B}]\frac{f_\mathrm{a}f_\mathrm{b}}{f_\mathrm{ab}}$, where $f_\mathrm{a}$, $f_\mathrm{b}$, and $f_\mathrm{ab}$ are activity coefficients for A, B, and the "activated complex" through which the reaction proceeds. Quantitative confirmation of such an expression has been possible only in ionic reactions in solvents of high dielectric constant where $f_\mathrm{ab}$ may be calculated by the Debye–Hückel law, but many attempts have been made to extend it, with varying success, to other reactions and media as well.[4]

Probably the simplest mechanism for thermal polymerization which is in keeping with the facts of organic chemistry is that of bimolecular initiation, growth, and termination with steps and rate expressions as follows, where M, M* and P are monomer, growing chain, and unreactive polymer, and the *f*'s the appropriate activity coefficients:

$$\text{Initiation: } 2\mathrm{M} \longrightarrow 2\mathrm{M}^* \qquad v_1 = k_1[\mathrm{M}]^2\frac{f_\mathrm{m}^2}{f_{2\mathrm{m}}} \qquad (1)$$

$$\text{Growth: } \mathrm{M}^* + \mathrm{M} \longrightarrow \mathrm{M}^* \quad v_2 = k_2[\mathrm{M}][\mathrm{M}^*]\frac{f_\mathrm{m}f_{\mathrm{m}^*}}{f_{\mathrm{mm}^*}} \qquad (2)$$

$$\text{Termination: } 2\mathrm{M}^* \longrightarrow 2\mathrm{P} \quad v_3 = k_3[\mathrm{M}^*]^2\frac{f_{\mathrm{m}^*}^2}{f_{2\mathrm{m}^*}} \qquad (3)$$

Application of the steady state principle to these equations yields, for the over-all rate

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = k_2\sqrt{\frac{k_1}{k_3}}[\mathrm{M}]^2 f_\mathrm{m}^2 [f_{2\mathrm{m}^*}/f_{\mathrm{mm}^*}^2 f_{2\mathrm{m}}]^{1/2} \qquad (4)$$

Equation (4) states that the rate of polymerization is second order in respect to monomer concentration in any given medium. How it will change with changing medium will depend upon variation in the various (immeasurable) activity coefficients, but three types of variation are experimentally distinguishable. (1) The ratio of all the activity coefficients remains sensibly constant, leading to a rate second order in respect to monomer *concentration.* In most discussions of polymerization kinetics this constancy is assumed, and it is further suggested by the statistical treatment of Flory.[5] (2) The ratio of activity coefficients of the activated complexes, $f_{2\mathrm{m}^*}/f_{\mathrm{mm}^*}^2 f_{2\mathrm{m}}$, remains constant, but the activity coefficient of the monomer varies leading to a rate second order in respect to monomer *activity.* (3) Neither of the above ratios remains constant. Here, the polymerization rate would not be a simple function of any measurable quantity.

In the case of the initial thermal polymerization of styrene in hydrocarbons, (1) at first appears the correct alternative since smooth, consistent second order rates are obtained. However, monomer activity and concentration are nearly enough identical in the system studied to make it impossible to rule out alternative (2). In the thermal polymerization of styrene to high extents of reaction, on the other hand, a choice is possible, since a wide variation between monomer concentration and activity takes place. Accord-

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(1) (a) Suess, Pilch and Rudorfer, *Z. physik. Chem.*, **179A**, 361 (1937); (b) Dostal and Jorde, *ibid.*, **179A**, 23 (1937); (c) Suess and Springer, *ibid.*, **181A**, 81 (1937); (d) Schulz and Husemann, *ibid.*, **36B**, 184 (1937); (e) Schulz, Dinglinger and Husemann, *ibid.*, **43B**, 47, 385 (1939); also unpublished work carried out in this Laboratory by R. A. Gregg and F. M. Lewis.

(2) Flory, THIS JOURNAL, **59**, 241 (1937).

(3) Brønsted, *Z. physik. Chem.*, **102**, 109 (1922).

(4) For a detailed discussion with many references, Ch. VIII, Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(5) Flory, *J. Chem. Phys.*, **12**, 425 (1944).