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Thermal Degradation of Fractionated High and Low Molecular Weight Polystyrenes[1]

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In previous work on the thermal degradation of polystyrene of average molecular weight of 230,000, carried out in a vacuum in the temperature range 318 to 348 °C, the rate curves exhibited distinct maximums when percentage loss of sample per minute was plotted as a function of percentage volatilization. These maximums correspond to a volatilization of about 35 to 45 percent and tend to flatten with decreased temperature of pyrolysis. A similar study of rates of thermal degradation at 307.5 °C has now been made on two groups of polymers: (1) low molecular weight, 24,000; 51,000; and 66,000; and (2) high molecular weight, 2,000,000; 2,250,000; and 5,000,000. Whole polymers and also fractions of narrow-range molecular weight were used. The rate curves for the 24,000 and 51,000 molecular-weight samples exhibit very high initial rates, but no maximums; the 66,000 sample showed a maximum at 45 percent volatilization. The rate curves for the 2,000,000, 2,250,000, and 5,000,000 molecular-weight samples exhibit a gradual rise up to about 25 percent volatilization; then, instead of forming maximums, they follow plateaus to about 50 percent volatilization. These plateaus are indicative of a zero-order reaction in the range that they cover, and the rates corresponding to them fit well on the Arrhenius activation-energy curve obtained previously for polystyrene samples at higher temperatures.

1. Introduction

The rates of thermal degradation of polystyrene in a vacuum have been studied extensively by Jellinek [1,2],[2] Madorsky [3,4], and Grassie [5,6]. However, the exact mechanism of degradation has been uncertain. The reaction does not follow a simple process of random initiation or end initiation. Instead, there appears to be a complex mechanism that has been explained by assuming random initiation, with a considerable amount of intramolecular and intermolecular transfer of free radicals, accompanied by unzipping at free-radical chain ends [7,8,9]. In addition to this, structural irregularities, so-called "weak links," in the backbone of the chains have been postulated to account for some of the degradation of the chains [1,2,5,6].

In the earlier studies on thermal degradation a polystyrene sample of molecular weight 230,000 (osmotic pressure) was pyrolyzed in the temperature range of about 330 to 400 °C. Curves of the rates of degradation in percent of original sample plotted as a function of percentage degradation exhibit maximums in the range of about 35 to 45 percent degradation [3]. These curves approach a horizontal line at decreased temperatures of degradation, as shown in figure 1. At 299.5 °C the middle portion of the rate curve approaches very closely a horizontal line [4], which is indicative of a zero-order reaction. Thus, although at the higher temperatures the mechanism of reaction is rather complicated, it seems to approach a zero-order at low temperatures. In order to elucidate this mechanism a series of experiments were carried out at relatively low temperatures, using polystyrene samples of high purity, fractionated and unfractionated, and of both high and low molecular weight.

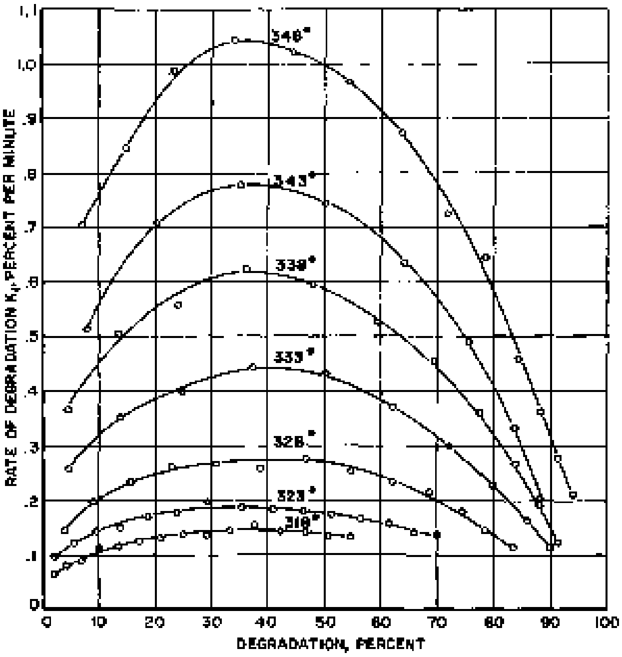

FIGURE 1. *Rates of thermal degradation of unfractionated polystyrene of molecular weight of 230,000.*

Rate of sample loss, K_1 is measured in percent of original sample. Figure is taken from references [3] and [4].

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[1] This paper was presented at the 141st meeting of the American Chemical Society in Washington, D.C., March 20–29, 1962.

[2] Figures in brackets indicate the literature references at the end of this paper.

2. Apparatus and Experimental Procedure

In earlier studies on rates of thermal degradation of polymer a tungsten helical spring microbalance was used for the higher temperatures; in the present work an Elmic electronic microbalance was used because it was more suitable for measurements of the slower rates obtained at the relatively low temperature of 307.5 °C. This electronic balance automatically recorded the temperature and loss of weight of the sample, and could be operated for long periods of time without attention.

The experimental procedure using this balance has been described in detail [4]. A 4 to 5 mg sample of the polymer in a small platinum crucible was suspended from the arm of the balance enclosed in a glass housing. The system was evacuated to about 10^{-4} mm Hg. An electric furnace which was preheated to the required temperature was then raised around the glass housing for pyrolysis of the sample. A chromel-chromel constantan thermocouple directly under the crucible reached the operating temperature in about 15 min. Very little loss of weight occurred during the warming-up period. The thermocouple was precalibrated against a similar thermocouple placed in the crucible in contact with its bottom. The temperature was kept constant to within ±0.2 °C by means of an electronic thermostat.

3. Materials

Eastman styrene, stabilized with *p-tert*-butylcatechol, was used in the preparation of the polymer. It was first washed with 7 percent NaOH, then with distilled water, and finally dried with $CaSO_4$. The dried monomer was distilled at 18 mm Hg. The purified dry monomer was degassed in a high-vacuum line and distilled into dilatometers. Two batches of polymers were prepared: polymer A and polymer B. No initiator was used for either of these two polymers.

Polymer A: This polymer was polymerized for a year at room temperature to about 50 percent conversion. The reaction mixture was poured into methanol. The precipitated polymer was then dried. The viscosity-average molecular weight of the whole polymer was 2,250,000. The fractionation was begun at a concentration of 0.5 percent of polymer in methyl ethyl ketone using isopropyl alcohol as a precipitant. Several fractions and subfractions were recovered.

Polymer B: This polymer was polymerized at 180 °C to about 30 percent conversion. The reaction mixture was poured into methanol and then precipitated with water. The viscosity-average molecular weight of the whole polymer was 51,000. Fractionation began with an initial concentration of 0.6 percent of the polymer in a methyl-ethyl ketone acetone mixture (1:1) using methanol as a precipitant. Twelve fractions were recovered.

Pertinent data on the unfractionated and fractionated materials used in this paper are shown in table 1. The molecular weights of these materials were determined by the viscosity method. The intrinsic viscosities were determined in benzene at 40 °C using an Ubbelohde viscometer. Molecular weights were calculated from the relation

TABLE 1. *Polystyrene samples used in pyrolysis*

Sample No.	Fraction	Mol. wt.
A-uf	Unfractionated	2,250,000
A-hf	High fraction	5,000,000
A-lf	Low fraction	2,000,000
B-uf	Unfractionated	51,000
B-hf	High fraction	66,000
B-lf	Low fraction	24,000

$$[\eta]=1.00\times10^{-4}\cdot M_w^{0.75}$$

which is very close to the relation given by Flory [10] for the intrinsic viscosity and weight-average molecular weight of fractions of polystyrene.

4. Experimental Work

4.1. Molecular Weight of Degraded Polymers

Samples of polystyrene fraction A-lf, molecular weight 2,000,000 (table 1), were pyrolyzed in a vacuum for various periods of time at temperatures ranging from 304 to 312 °C. The residues were dissolved in benzene and freeze-dried prior to determining their average molecular weight by viscosity and osmotic-pressure methods.

The viscosity method has been described above. The osmotic-pressure determinations were made in cyclohexane at 35 °C in Stabin osmometers using "never-dried" gel cellophane No. 600. Results of these pyrolysis experiments are shown in table 2. In figure 2 the results of molecular weight determinations of the residues by the viscosity and the osmotic-pressure methods for sample A-lf are compared with similar results obtained previously [3] using the osmotic-pressure method for an unfractionated thermally prepared polystyrene sample of molecular weight 230,000. The results indicate a rapid drop of molecular weight during the initial 10 percent loss of weight to about 70,000 to 80,000. This drop is similar for both the fractionated polystyrene of average molecular weight 2,000,000 and the unfractionated sample of molecular weight 230,000. Beyond 10 percent loss the drop is less drastic and the curve shows a tendency to level off at about 50,000 (osmotic-pressure molecular weight) for both polymers.

TABLE 2. *Molecular weights of degraded polystyrene fraction A-lf*

Temp.	Duration	Volatilization	M_v(visc.)	M_n(os. pr.)	M_v/M_n
°C	min	%			
304	150	1.3	335,000	200,000	1.66
312	240	5.7	168,000	98,600	1.70
310	560	16.6	90,600	61,100	1.48
304	960	41.0	65,000	36,600	1.78
310	1260	51.0	50,400	30,600	1.63
310	1500	61.0	41,000	25,600	1.60
Average					1.64

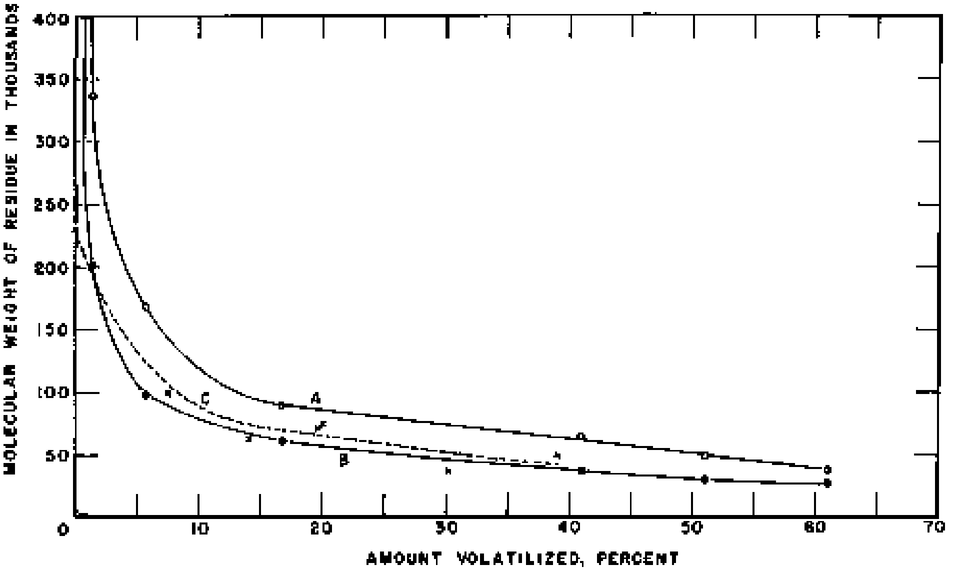


Figure 2. *Drop in the molecular weight of polystyrene, fraction A-lf, molecular weight 2,000,000*

A—by the viscosity method; B—by the osmotic-pressure method. Curve C is from earlier work [3], for unfractionated polymer, molecular weight 230,000 by the osmotic-pressure method.

4.2. Rates of Degradation

The whole polymers A and B, and their two fractions (table 1) were studied. Pertinent details of the rate experiments are shown in table 3. In figure 3 cumulative loss of weight, in percent of sample, is plotted as a function of time. Fractions A-hf and A-lf of 5,000,000 and 2,000,000 molecular weight, respectively, show the same pyrolysis curve. These high molecular-weight curves show inflexions and resemble those obtained previously for unfractionated, thermally prepared polystyrene, molecular weight, 230,000, and of two fractions from this polymer of molecular weights 106,000 and 584,000 [3].

Table 3. *Rates of degradation of polystyrene at 307.5 °C*

Sample No.	Mol. wt.	Duration	Volatilization	Max. rate
		hr	*%*	*%/min*
A-uf	2,250,000	30	73.0	0.0480
A-hf	5,000,000	30	62.5	.0450
A-lf	2,000,000	30	62.5	.0450
B-uf	51,000	22	74.0	a.0645
B-hf	66,000	30	73.0	.0584
B-lf	24,000	22	73.0	.0690

a This rate corresponds to an inflection on the rate curve instead of to a maximum rate.

In figure 4 the rates, calculated from the curves in figure 3, are plotted in percent of sample volatilized per minute as a function of percentage volatilized. The high molecular weight polymers, both unfractionated and fractionated, show a gradual rise in rate up to about 25 percent loss, then there is a plateau extending to about 50 percent loss, followed by a drop in rate tending toward zero at 100 percent volatilization. The rate curve for B-hf fraction, 66,000 molecular weight, resembles those for the high molecular weight polymers, except that it does not have a plateau. The 24,000 B-lf fraction indicates a constant rate up to about 30 percent volatilization, followed by a drop toward 100 percent volatilization. The 51,000 B-uf sample starts at a very high rate and exhibits a pronounced inflexion between 40 to 45 percent volatilization, followed by a gradual decrease in rate.

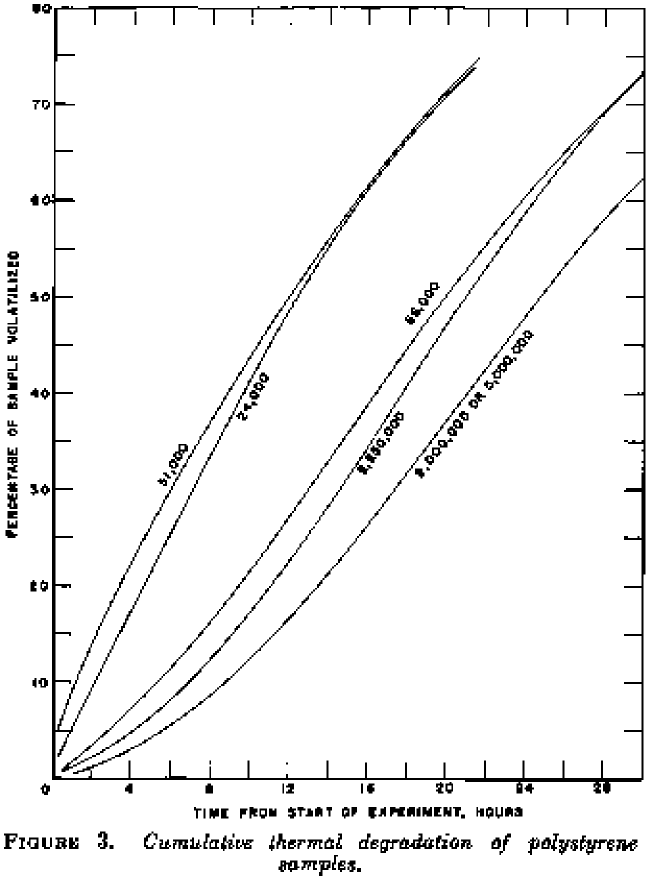


Figure 3. *Cumulative thermal degradation of polystyrene samples.*

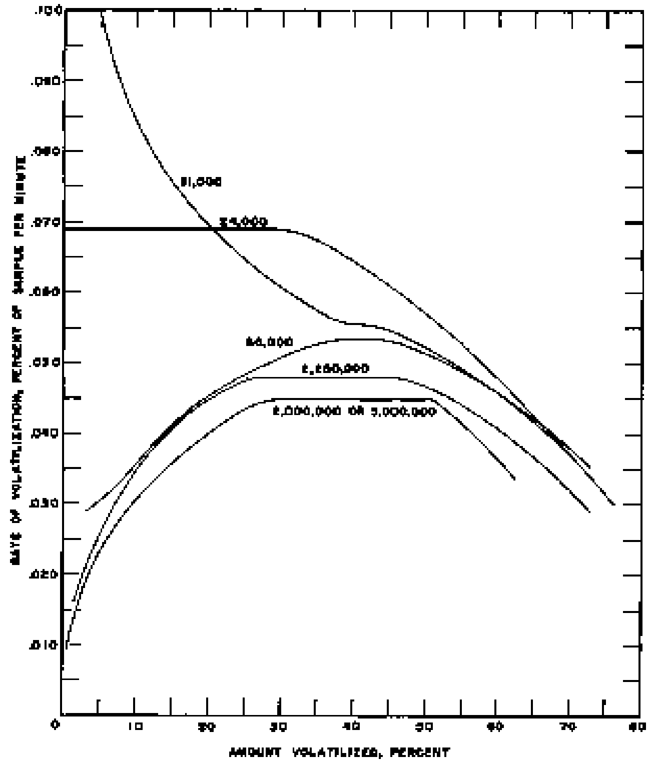


Figure 4. *Rates of thermal degradation of polystyrene samples.*

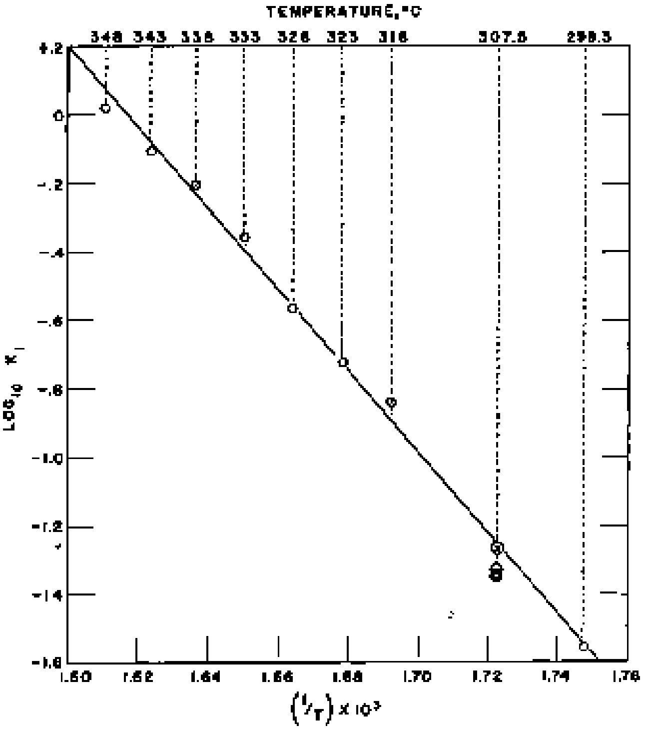
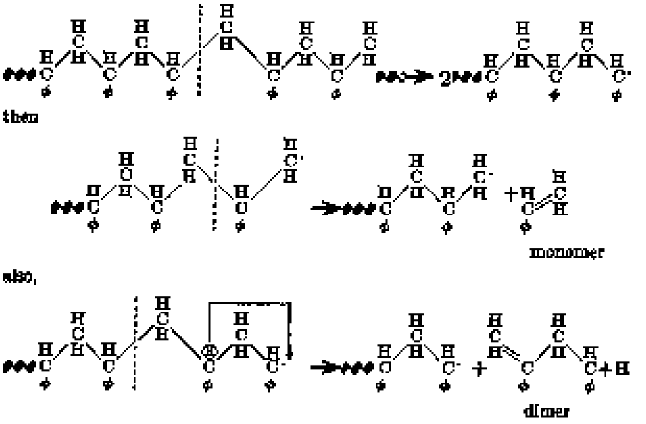


Figure 5. *Arrhenius plot for the rates of thermal degradation of polystyrene.*

○—Polystyrene molecular weight 230,000
⊗—Polystyrene sample B-hf
△—Polystyrene sample A-lf
⊚—Polystyrene sample A-hf and A-lf

5. Discussion

As the high molecular weight polystyrene undergoes pyrolysis, its (*M*) drops rapidly during the first 5 to 10 percent loss of weight and stabilizes at about 40,000 to 60,000. The level of stabilization seems to be independent of the initial molecular weight or of the molecular distribution in the polymer species, provided the initial (*M*) is not below the stabilization level. The initial drop in molecular weight may be due partially to scissions at weak-link bonds caused by impurities in the polymers, but is mainly due to thermal scissions in the chain. This continues to a point where the drop in weight caused by random scissions is counter-balanced by the disappearance of smaller chains through unzipping, mainly into monomers. According to Staudinger and Steinhofer [11] and Madorsky and Straus [12], the degradation products from polystyrene consist of about 40 percent monomers, 20 percent dimer, 20 percent trimer, and some larger fragments. Unzipping takes place at free-radical chain ends, presumably as follows:



At this point stabilization sets in. Since loss here is mainly due to loss by unzipping at ends of chains, the rate is constant as long as the number of chain ends stays constant. This explains the plateau in the rate curves of the high molecular weight species. However, the average molecular weight drops gradually during this period, as is indicated in figure 2. Thus, as shown in figure 4, the portions of the rate curves from about 25 to 50 percent weight loss in the case of the three highest molecular weight samples point to a zero-order reaction. Beyond 50 percent volatilization a decrease in rate takes place due to a decrease in the number of chain ends. This is predicated on the assumption that in the range of conversion of 25 to 50 percent, the rate of disappearance of chain-ends by unzipping is equal to the rate of formation of new chain ends through random scission, while in the initial and final stages, the rate of disappearance of chains is respectively slower or faster than the rate of formation of new chain ends.

In the thermal degradation at 299.3 °C of unfractionated polystyrene of molecular weight 230,000, the rate curve shows a plateau in the range of about

20 to 50 percent volatilization [4]. However, at higher temperatures, 318 to 348 °C, the rate curves for this polymer show maxima instead of plateaus at about 35 to 45 percent volatilization [3]. This could be explained on the ground that with the rise in the temperature of pyrolysis the various reactions involved are speeded up and overlap so that the region of stabilization narrows down from a plateau to a peak.

Simha and Wall [8] predict, on theoretical grounds, the occurrence of maximums in the rate curves for the thermal degradation of polystyrene at about 25 percent degradation, in disagreement with the present and the earlier work.

Polystyrene fraction B-hf has a molecular weight (66,000) which is in the region at which stabilization occurs. Although the temperature of degradation is low enough for a plateau to occur, stabilization of molecular weight and of rate of loss of weight is of short duration and they begin to drop soon after stabilization sets in. As a result, the curve in figure 4 exhibits a maximum instead of a plateau. The whole polymer, B-uf, molecular weight 51,000, has apparently a large proportion of very short chains. The curve shows a high initial rate, followed by a short interval of stabilization at about 40 percent volatilization. From here on, this curve follows the same trend as the other curves. Low fraction B-lf, molecular weight 24,000, apparently has a narrow molecular weight distribution and is free from very short chain molecules. It decomposes initially in a manner of a zero-order reaction, but at a high rate, up to about 30 percent loss. Beyond this, the rate drops gradually due to the disappearance of some of the shorter molecules, while few scissions occur to compensate for the decrease in the number of chain ends.

Figure 5 represents an Arrhenius plot for the activation energy of the thermal degradation of polystyrene. The rate K_1 represents a rate of loss of weight in percent of the original sample per minute as a function of percentage volatilization. The points in this plot represent maximums of the rate curve shown in figure 1 for polystyrene of molecular weight 230,000, the peak of the rate curve shown in figure 4 for polymer fraction B-hf, and for the plateau rates in the same figure of polymer sample A-uf and its fractions, A-hf and A-lf. The slope of the curve indicates an activation energy of 55 kcal/mole. A similar value was obtained by plotting initial K_2 rates for polystyrene of molecular weight 230,000 [3, 4]. The initial K_2 rates were obtained by extrapolating to zero the degradation rates expressed in percent of residue per minute as a function of percentage volatilization.

6. References

[1] H. H. G. Jellinek, J. Polymer Sci. **3,** 350 (1948).
[2] H. H. G. Jellinek, J. Polymer Sci. **4,** 13 (1949).
[3] S. L. Madorsky, J. Polymer Sci. **9,** 133 (1952).
[4] S. L. Madorsky, J. Research NBS **62,** 219 (1959).
[5] N. Grassie and W. W. Kerr, Trans. Faraday Soc. **53,** 234 (1957).
[6] N. Grassie and W. W. Kerr, Trans. Faraday Soc. **55,** 1050 (1959).
[7] R. Simha and L. A. Wall, J. Phys. Chem. **56,** 707 (1952).
[8] R. Simha, L. A. Wall, and J. Bram, J. Chem. Phys. **29,** 894 (1958).
[9] S. Straus and S. L. Madorsky, J. Research NRS **65A** (Phys. and Chem.) 243 (1961).
[10] P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, p. 312, (1953).
[11] H. Staudinger and A. Steinhofer, Ann. Chemie **517,** 35 (1935).
[12] S. L. Madorsky and S. Straus, J. Research NBS **40,** 417 (1948).

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