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# KINETICS OF RADICAL POLYMERIZATION. I. INVESTIGATION OF THE RADICAL BULK POLYMERIZATION OF VINYL ACETATE BY THE ROTATING SECTOR METHOD

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## ABSTRACT

The chain propagation and termination rate coefficients of vinyl acetate radical polymerization were determined by the rotating sector method at 25°C. The values determined are in good agreement with those of Kwart, Matheson, and Swain. The chain termination rate coefficient essentially differs from that determined by Burnett.

## INTRODUCTION

Few data can be found in the literature for the rate constants of propagation ( $k_2$ ) and termination ( $k_4$ ) steps of the radical polymerization of vinyl acetate (VAc). Values

determined by the rotating sector method are collected in Table 1. There are some deviations among the  $k_2$  and  $k_4$  values listed in the table; these are presumably caused by the insufficient purity of the monomer.

The aim of the present work is to determine the absolute rate constants of chain propagation ( $k_2$ ) and termination ( $k_4$ ) of the radical bulk polymerization of VAc at 25°C by the rotating sector method. These experiments are a part of the investigation of radical bulk polymerization of VAc by the rotating sector method in a broader temperature range (20–50°C), aiming at the determination of the activation energies of elementary reaction steps.

## EXPERIMENTAL

The monomer used in the experiments (Fluka product) was purified as given in Ref. 6.

Prepolymerization, deoxygenation of the monomer, and filling into the ampules were carried out in the equipment published in Ref. 6. Prepolymerization of the monomer was controlled by a thermoelement, and the end of prepolymerization was determined by an increase of temperature of 5°C. Polymerization was carried out in cylindrical quartz cuvettes (HELMA product, FRG). The meniscus in the dilatometer tube (2 mm diameter) was followed at an accuracy of 0.01 mm. The rotating sector measurements were performed by the improved method of Nagy et al. [7, 8]. Benzoin was used as the photoinitiator. The substance was purified as given in Ref. 7.

The rate of volume contraction due to constant illumination and to different illumination times ( $W_{st}$  and  $W_{imp}$ ) were measured for each ampule. The best fitting of experimentally determined pairs of relative radical concentration values belonging to different illumination times to the theoretical sector curve was made by a HP 9845

TABLE 1. Literature Values of the Absolute Rate Constants of Chain Propagation and Termination of VAc as Determined by the Rotating Sector Method

$k_2$ , L·mol <sup>-1</sup> ·s <sup>-1</sup>	$k_4 \times 10^{-6}$ L·mol <sup>-1</sup> ·s <sup>-1</sup>	$(k_2/k_4)$ , $\times 10^6$	$T$ , °C	Ref.
556	3040	—	15.9	1
670	2500	—	15.9	2
700	2600	—	16	3
1100	80	—	25	4
1012	58.8	17.2	25	5
1000	59	16.9	25	10

B type computer, minimizing the square sums of deviations. The fitted sector curve obtained in this way is shown in Fig. 1.

### EXPERIMENTAL RESULTS AND THEIR EVALUATION

The  $k_2/k_4$  quotient was calculated from the sector curve by using

$$\frac{k_2}{k_4} = \frac{\bar{W}_{s1}}{m} \tau \quad (1)$$

where  $m$  is the monomer concentration, and  $\tau$  denotes the steady lifetime of radicals. In Table 2 the measured and fitted values of relative radical concentrations belonging to different illumination times are listed.

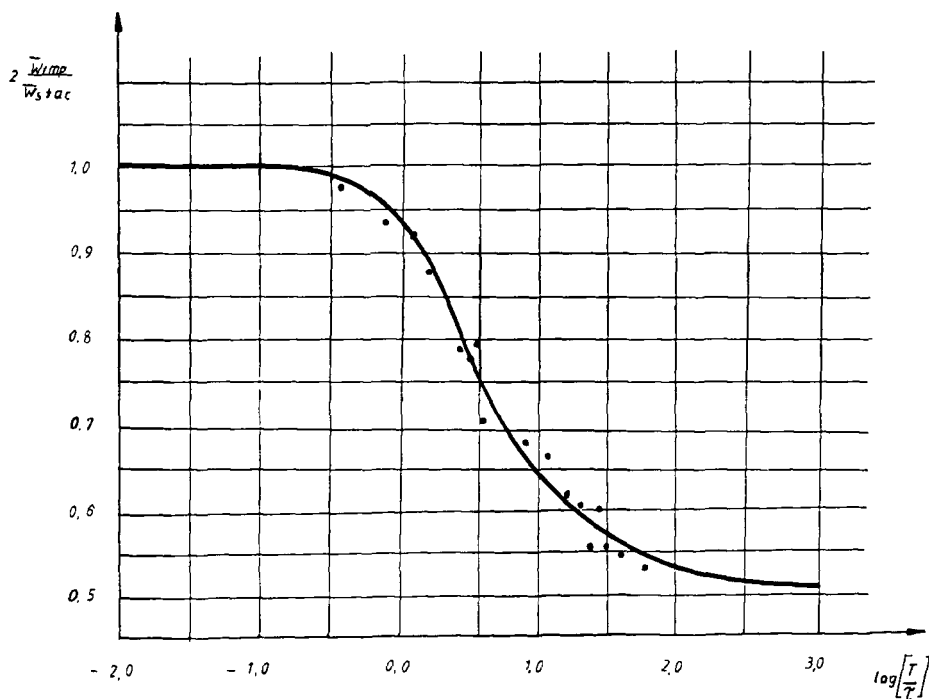


FIG. 1. Fitting of relative polymerization rates measured at different illumination times to the theoretical sector curve (sector ratio  $p = 3$ ).

TABLE 2. Relative Radical Concentrations Measured at Different Illumination Times (sector ratio  $p = 3$ ;  $\tau = 0.247$  s)

Illumination time, s	$2 \frac{\bar{r}_{\text{imp}}}{r_{\text{stac}}}$	
	Measured	Fitted
0.1	0.976	0.986
0.2	0.928	0.951
0.3	0.910	0.912
0.4	0.896	0.875
0.7	0.781	0.792
0.8	0.775	0.773
0.9	0.791	0.756
1	0.693	0.742
2	0.673	0.659
3	0.656	0.622
4	0.618	0.600
5	0.599	0.585
6	0.552	0.575
7	0.594	0.567
8	0.552	0.560
10	0.542	0.551
15	0.529	0.537

The rate constants change with increasing conversion, therefore the conversion was kept under 3% in all measurements in order to avoid conversion errors.

The error in radical lifetime ( $\tau$ ) determined this way was estimated as follows. The error in relative radical concentration is influenced by two factors: the error of  $\bar{W}_{\text{imp}}$  measured at different illumination times, which is about  $\pm 2\%$ , and the error of  $\bar{W}_{\text{st}}$  measured at constant illumination, which decreases proportionally by the square root of the number of measurements [8]. The rate of polymerization due to the constant illumination time was measured twice for each ampule, thus its error decreased to  $\pm 0.63\%$  (10 measurements). Thus, the total error gives an error interval of  $\pm 2.63\%$ , which means an error of 14.3% in the radical lifetime [8].

For the determination of absolute rate constants of chain propagation ( $k_2$ ) and termination ( $k_4$ ), the value of the  $k_2/\sqrt{k_4}$  is needed. It can be determined by investigation of the steady-state polymerization. Since there were no experimental data available at 25°C, the  $k_2/\sqrt{k_4}$  values were calculated using the equations published in Refs.

6 and 9. The equations used are the following. The temperature dependence of the overall rate constant is

$$K_0 = 1.35 \times 10^{11} \exp \left( - \frac{89,999}{RT} \right) \text{L}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{s}^{-1}. \quad (2)$$

The temperature dependence of the decomposition of the initiator (AIBN) [11] is

$$k_1 = 1.58 \times 10^{15} \exp \left( - \frac{128,930}{RT} \right) \text{s}^{-1}. \quad (3)$$

From Eqs. (2) and (3) we obtain

$$\frac{k_2}{\sqrt{k_4}} = \frac{(K_0)_{25^\circ\text{C}}}{\sqrt{(2k_1f)_{25^\circ\text{C}}}} = 0.1062, \quad (4)$$

where  $f = 0.536 \pm 0.018$  [9] in the radical efficiency factor.

By using the notation given in Ref. 7 ( $k_2/\sqrt{k_4} = 1/\delta$ ), the rate constant of chain propagation ( $k_2$ ) and of termination ( $k_4$ ), as well as their errors, can be determined by

$$k_2 = \frac{(k_2/\sqrt{k_4})^2}{k_2/k_4} \quad (5)$$

or, expressed by the measured quantities,

$$k_2 = \frac{m}{\bar{W}_{st} \delta^2 \tau} \quad (6)$$

and

$$\left| \frac{\Delta k_2}{k_2} \right| + \left| \frac{\Delta m}{m} \right| + \left| \frac{\Delta W_{st}}{W_{st}} \right| + 2 \left| \frac{\Delta \delta}{\delta} \right| + \left| \frac{\Delta \tau}{\tau} \right|. \quad (7)$$

The error in  $k_2/\sqrt{k_4}$  determination is generally  $\pm 2.63\%$  [6]. Monomer concentration can be measured precisely, thus the error originating from this can be neglected.

$$\frac{\Delta k_2}{k_2} = 0.63 + (2)(2.63) + 14.9 = 20.79\%,$$

$$k_4 = \left[ \frac{k_2 \sqrt{k_4}}{k_2/k_4} \right]^2, \quad (8)$$

or, expressed by the measured quantities,

$$k_4 = \left[ \frac{m}{W_{st} \delta \tau} \right] \quad (9)$$

and

$$\left| \frac{\Delta k_4}{k_4} \right| = 2 \left[ \left| \frac{\Delta m}{m} \right| + \left| \frac{\Delta W_{st}}{W_{st}} \right| + \left| \frac{\Delta \delta}{\delta} \right| + \left| \frac{\Delta \tau}{\tau} \right| \right], \quad (10)$$

$$\frac{\Delta k_4}{k_4} = 2(0.63 + 2.63 + 14.9) = 36.32\%.$$

The absolute rate constants determined by Eqs. (5) and (8) are

$$k_2 = 755.8 \pm 162.7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1},$$

$$k_4 = (50.18 \pm 18.6) \times 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}.$$

The rate constants obtained this way are in good agreement with the literature values at 25°C listed in Table 1. The very high  $k_4$  values determined by Burnett [1, 2] seem completely improbable. They might be due to insufficient purification of the monomer.

The determination of absolute rate constants at other temperatures and the activation energies of elementary reaction steps will be treated in a following paper.

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