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### Kinetics of Radical Polymerization. LII. Kinetic Investigation of Styrene Polymerization in Viscous Medium

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# KINETICS OF RADICAL POLYMERIZATION. LII. KINETIC INVESTIGATION OF STYRENE POLYMERIZATION IN VISCOUS MEDIUM

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## ABSTRACT

This paper deals with the homopolymerization of the systems styrene–azobisisobutyronitrile–dibutyl phthalate–50°C and styrene–benzoin–dibutyl phthalate–50°C. The dependencies of initiation and overall rates of the polymerization on the concentrations of monomer and the viscous solvent were studied. The absolute rate constants for chain propagation and termination were determined. The termination rate constant of the styrene–dibutyl phthalate system was found to be inversely proportional to the viscosity of the medium. The propagation rate constant was found to decrease with monomer concentration, which could be evaluated quantitatively in terms of the hot radical theory.

## INTRODUCTION

In order to clarify the effect of viscosity on radical polymerization, in a previous paper [1] we studied the kinetics of methyl methacrylate polymerization in a viscous solvent. The present work deals with the kinetics of styrene polymerization under analogous conditions.

The propagation ( $k_2$ ) and termination ( $k_4$ ) rate constants of styrene were deter-

mined by Burnett et al. [2] at 25 and 60°C. In the course of kinetic investigations they used four solvents, and the common viscosities of the mixtures varied between  $4.74 \times 10^{-4}$  and  $5.86 \times 10^{-3}$  Pa·s at 60°C. The rate constants were determined for every solvent only at 2–3 monomer concentrations. By a comparison of the  $k_2$  and  $k_4$  values obtained in the four systems, they found the value of the propagation rate constant to decrease slightly with an increase of solvent concentration.

The value of the termination rate constant is inversely proportional to the viscosity of the monomer–solvent mixture, in accordance with the diffusion theory of North [3, 4].

The rate of solvent viscosity—its effect on the elementary steps of polymerization and on the rate constants—can be more precisely studied within a single system by using an inert solvent and investigating a broad range of concentrations. By using this method, differences caused by changes of solvent and other possible complications (e.g., side reactions) can be avoided.

In our present work we report on polymerization kinetic investigations carried out in a viscous solvent (dibutyl phthalate). The initial viscosities of the polymerization mixtures within a system vary between  $5.25 \times 10^{-4}$  and  $3.98 \times 10^{-3}$  Pa·s.

In our experiments the variations of the overall and the initiation rate constants of polymerization were studied for their dependence on the monomer concentration. The values of chain propagation and termination rate constants were determined, i.e., the effect of the medium on the corresponding constants were investigated.

## EXPERIMENTAL

Purification of dibutyl phthalate (DBPh) was reported previously [1], as was that of styrene (St) and azobisisobutyronitrile (AIBN) [5, 6]. In investigations with the rotating sector method, the commonly used photoinitiator benzoin was applied, the purification of which was also given earlier [7, 10]. The purities of the materials used were checked by measuring their refractive indexes and melting points: styrene (St),  $n_D^{20} = 1.5465$ ; dibutyl phthalate (DBPh),  $n_D^{20} = 1.4922$ ; azobisisobutyronitrile (AIBN), mp 103.5–104°C; benzoin, mp 135–136°C.

Polymerization kinetic measurements were carried out dilatometrically at 50°C. The rate of initiation was determined by the inhibition method by using the stable free radical triphenyl verdazyl (TPV). TPV was prepared according to Ref. 8. Viscosities were measured in an Ubbelohde viscometer at 50°C.

## RESULTS AND THEIR EVALUATION

The initial viscosities of St–DBPh mixtures used in the investigations of St–AIBN–DBPh–50°C and St–benzoin–DBPh–50°C polymerization systems are list-

ed in Table 1. The experimental points can be well approximated by a quadratic polynomial:

$$10^3\eta = 6.36 - 10.81\chi_{St} + 5.02\chi_{St}^2 \text{ (Pa}\cdot\text{s)} \quad (1)$$

The viscosity value of a given dilution was calculated by Eq. (1).

The value of the initial rate constant ( $2k_1f$ ) was determined at various monomer concentrations by using TPV. For polymerization initiated by a stable free radical, the rate constant of initiation can be determined by

$$t_i = \frac{\mu}{2k_1f} \frac{z_0}{\bar{x}} \quad (2)$$

where  $t_i$  denotes the length of the inhibition period,  $\mu$  is the stoichiometric coefficient of the inhibitor (its value is unity for a stable free radical),  $z_0$  stands for the initial concentration of the inhibitor, and  $\bar{x}$  is the initiator concentration during the inhibition period. A side reaction was found to take place between the inhibitor and the monomer as has been pointed out in the inhibition kinetic investigation of monomers of higher reactivity [9, 14]. In such cases the  $t_i = f(z_0/\bar{x})$  function is not linear.

If only the above-mentioned pseudounimolecular side reaction takes place in

TABLE 1. Viscosities ( $\eta$ ) of the Initial Mixture in the System St-DBPh as a Function of the Mole Fraction of the Monomer ( $\chi_{St}$ ) at 50°C

|    | $\chi_{St}$ | $10^3\eta_{meas}$ , Pa·s | $10^3\eta_{calcd}$ , Pa·s |
|----|-------------|--------------------------|---------------------------|
| 1  | 0           | 6.401                    | 6.360                     |
| 2  | 0.247       | 3.976                    | 3.996                     |
| 3  | 0.288       | 3.640                    | 3.663                     |
| 4  | 0.330       | 3.326                    | 3.339                     |
| 5  | 0.385       | 2.920                    | 2.942                     |
| 6  | 0.463       | 2.421                    | 2.430                     |
| 7  | 0.579       | 1.805                    | 1.783                     |
| 8  | 0.697       | 1.314                    | 1.262                     |
| 9  | 0.775       | 1.053                    | 0.995                     |
| 10 | 1.00        | 0.525                    | 0.566                     |

addition to the one-step inhibition reaction, the rate constant of initiation can be determined by the following linear approximation formula:

$$\left(\frac{z_0}{x_0 t_i}\right)^{3/2} = (2k_1 f)^{3/2} \left[1 + 0.74 \left(\frac{2k' m - k_1}{2k_1 f}\right) \frac{z_0}{x_0}\right] \quad (3)$$

As can be seen from the measured data,  $2k_1 f$  is a linear function of the mole fraction of styrene at 50°C:

$$10^6 \cdot 2k_1 f = 1.805 \chi_{St} + 1.138 \quad (\text{s}^{-1}) \quad (4)$$

The  $2k_1 f$  values calculated by the function and the measured ones are listed in Table 2.

TABLE 2. Inhibition Kinetic Data of the Polymerization System St-AIBN-DBPh at 50°C

|   | $\chi_{St}$ | $10^2(z_0/x_0)$ | $t_i$ , min | $10^6 \cdot 2k_1 f_{\text{meas}}$ , s <sup>-1</sup> | $10^6 \cdot 2k_1 f_{\text{calcl}}$ , s <sup>-1</sup> |
|---|-------------|-----------------|-------------|---|--|
| 1 | 0.206       | 0.633           | 148.5       | 1.55  | 1.51   |
|   |             | 3.254           | 268         |   |  |
|   |             | 8.072           | 939.5       |   |  |
| 2 | 0.451       | 3.814           | 322         | 1.87  | 1.95   |
|   |             | 5.760           | 480         |   |  |
|   |             | 7.383           | 576         |   |  |
|   |             | 8.907           | 724         |   |  |
| 3 | 0.585       | 3.233           | 216         | 2.22  | 2.19   |
|   |             | 4.882           | 322         |   |  |
|   |             | 6.518           | 412.5       |   |  |
|   |             | 5.648           | 504         |   |  |
| 4 | 0.739       | 3.026           | 152         | 2.49  | 2.47   |
|   |             | 4.437           | 232         |   |  |
|   |             | 5.803           | 303         |   |  |
|   |             | 7.206           | 360         |   |  |
|   |             | 3.078           | 162         |   |  |
| 5 | 0.844       | 4.967           | 232         | 2.68  | 2.66   |
|   |             | 6.279           | 286         |   |  |
|   |             | 7.898           | 356         |   |  |
|   |             | 3.249           | 157         |   |  |
|   |             | 4.633           | 208         |   |  |
| 6 | 0.894       | 6.271           | 275         | 2.77  | 2.75   |
|   |             | 8.568           | 348         |   |  |
|   |             |                 |             |   |  |
| 7 | 1.0         |                 |             | 2.97  | 2.94 [15]  |

From these, we measured the overall rate constant of polymerization ( $K$ ) over a broad range of monomer concentration. As is known:

$$-\frac{dm}{dt} = K\sqrt{x_0}m \quad (5)$$

where  $m$  is the monomer concentration, and

$$K = \bar{k}_2 \sqrt{\frac{2k_1f}{k_4}} \quad (6)$$

With knowledge of the rate constant of initiation, the values of  $\bar{k}_2/\sqrt{k_4}$  can be calculated from  $K$ . These data are given in Table 3.

In order to be able to apply various monomer concentrations in different series of experiments, we attempted to give the experimentally observed  $\bar{k}_2/\sqrt{k_4}$  function with a suitable interpolation formula. The experimental data could well be approximated by a quadratic polynomial:

$$10^2 \frac{\bar{k}_2}{\sqrt{k_4}} = 2.97 - 1.59\chi_{St} + 0.53\chi_{St}^2 \quad (7)$$

The constants of the equation were determined by the method of nonlinear least squares.

TABLE 3. Kinetic Data for the Polymerization System St-AIBN-DBPh at 50°C

|    | $\chi_{St}$ | $10^2x_0$ ,<br>mol/L | $10^6W$ ,<br>$L^{-1}\cdot mol^{1/2}\cdot s^{-1}$ | $10^5K$ ,<br>$mol^{-1/2}\cdot L^{1/2}\cdot s^{-1}$ | $10^2k_2/\sqrt{k_4}$ ,<br>$L^{1/2}\cdot mol^{-1/2}\cdot s^{-1/2}$ |
|----|-------------|----------------------|--|--|---|
| 1  | 0.354       | 4.734                | 2.967  | 3.140  | 2.477   |
| 2  | 0.499       | 4.950                | 3.217  | 3.306  | 2.317   |
| 3  | 0.585       | 5.506                | 3.334  | 3.272  | 2.220   |
| 4  | 0.601       | 4.884                | 3.167  | 3.300  | 2.205   |
| 5  | 0.670       | 4.700                | 3.251  | 3.453  | 2.143   |
| 6  | 0.739       | 5.801                | 3.417  | 3.267  | 2.087   |
| 7  | 0.748       | 4.207                | 2.933  | 3.293  | 2.080   |
| 8  | 0.844       | 5.581                | 3.285  | 3.202  | 2.009   |
| 9  | 0.855       | 4.182                | 2.880  | 3.243  | 2.001   |
| 10 | 0.894       | 5.559                | 3.300  | 3.223  | 1.975   |
| 11 | 0.903       | 4.174                | 2.917  | 3.288  | 1.951   |
| 12 | 0.950       | 5.019                | 3.249  | 3.340  | 1.938   |
| 13 | 1.0         | 4.855                | 3.284  | 3.432  | 1.908   |

The absolute rate constants of the elementary steps of polymerization were determined by means of rotating sector polymerizing equipment. The construction of the rotating sector device, the evaluation of experimental data, and the calculation of error are given in detail in our previous papers [10, 11]. The rotating sector measurements make it possible to determine the average lifetime ( $\tau$ ) of propagating polymer radicals and, with this knowledge, to calculate the  $\bar{k}_2/\sqrt{k_4}$  ratios:

$$\frac{\bar{k}_2}{k_4} = \frac{W_{st}}{m} \tau \quad (8)$$

where  $W_{st}$  is the rate of polymerization measured under continuous illumination. The absolute rate constants can be calculated from  $\bar{k}_2/\sqrt{k_4}$  since

$$k_4 = \left( \frac{\bar{k}_2/\sqrt{k_4}}{k_2/k_4} \right)^2 \quad \text{and} \quad \bar{k}_2 = \frac{(\bar{k}_2/\sqrt{k_4})^2}{k_2/k_4} \quad (9)$$

The measured values are listed in Table 4.

Introducing the notation  $\bar{k}_2/\sqrt{k_4} = 1/\delta$  and considering Eq. (7), the relative error of absolute rate constants from the results of rotating sector measurements are

$$\frac{\Delta k_4}{k_4} = 2 \left\{ \left| \frac{\Delta m}{m} \right| + \left| \frac{\Delta W_{st}}{W_{st}} \right| + \left| \frac{\Delta \delta}{\delta} \right| + \left| \frac{\Delta \tau}{\tau} \right| \right\} \approx 0.375$$

0    0.0095    0.018    0.16

and

$$\left| \frac{\Delta k_2}{k_2} \right| = \left| \frac{\Delta m}{m} \right| + \left| \frac{\Delta W_{st}}{W_{st}} \right| + 2 \left| \frac{\Delta \delta}{\delta} \right| + \left| \frac{\Delta \tau}{\tau} \right| \approx 0.206$$

0    0.0095    2·0.018    0.16

In our case, the average error of polymerization rate determinations was  $\pm 1.9\%$ . Since the value of  $W_{st}$  was measured at least four times in a series of measurements, its error is half of the above value:  $\pm 0.95\%$ . The relative rate is indicated on the ordinate of the sector curve, the error of which is, following from the above,  $1.9 \pm 0.95 = 2.85\%$ . This value can cause an error of 16% in the determination of  $\tau$ . Thus, in the system St-DBPh the relative error of  $k_4$  is 37.5% while that of  $k_2$  is 20.6%.

It can be seen from our experimental results (see Table 4) that the constant value of the termination rate constant is (within the limits of experimental error) inversely proportional to the viscosity of the medium, in accordance with the results

TABLE 4.

| $\chi_{St}$ | $10^3 \eta_b$ ,<br>Pa·s | $\eta^{-1}$ ,<br>Pa <sup>-1</sup> ·s <sup>-1</sup> | $10^2 k_2 \sqrt{k_4}$ ,<br>L <sup>1/2</sup> ·mol <sup>-1/2</sup> ·s <sup>-1/2</sup> | $10^9 k_2/k_4$    | $k_2$ ,<br>L·mol <sup>-1</sup> ·s <sup>-1</sup> | $10^{-7} k_4$ ,<br>L·mol <sup>-1</sup> ·s <sup>-1</sup> | $10^{-4} k_4^0 = k_4 \eta_b$ ,<br>Pa·L·mol <sup>-1</sup> |                   |
|-------------|-------------------------|--|---|-------------------|---|---|--|-------------------|
| 1           | 0                       | 6.401  | 156 <sup>a</sup>  | 2.97 <sup>a</sup> | 8.01 <sup>a</sup>                               | 110.2 <sup>b</sup>                                      | 1.38 <sup>a</sup>  | 8.82 <sup>a</sup> |
| 2           | 0.316                   | 3.380  | 296   | 2.52              | 6.04  | 105.0   | 1.74   | 5.88              |
| 3           | 0.321                   | 3.344  | 299   | 2.51              | 5.43  | 116.3   | 2.14   | 7.16              |
| 4           | 0.504                   | 2.199  | 455   | 2.30              | 4.24  | 124.8   | 2.94   | 6.47              |
| 5           | 0.621                   | 1.641  | 609   | 2.18              | 4.02  | 118.5   | 2.95   | 4.84              |
| 6           | 0.807                   | 0.983  | 1017  | 2.03              | 3.13  | 131.5   | 4.20   | 4.26              |
| 7           | 0.906                   | 0.687  | 1456  | 1.97              | 2.45  | 158.0   | 6.45   | 4.43              |
| 8           | 0.951                   | 0.620  | 1618  | 1.94              | 2.26  | 166.0   | 7.34   | 4.55              |
| 9           | 1.0                     | 0.525  | 1905  | 1.91              | 1.90  | 190.0 <sup>b</sup>                                      | 9.91   | 5.20              |
|             |                         |  |   |                   |   |   | Mean value: $5.73 \pm 1.43$                              |                   |

<sup>a</sup>Values extrapolated to infinite dilution.<sup>b</sup>Literature data.

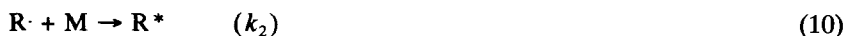


of Burnett et al. [2] as well as the diffusion theory of North [3, 4].

The data of Table 4 indicate that the propagation rate constant continuously decreases with dilution.

As is known, the hot radical theory [12] interprets deviations from classical kinetic rates by the special mechanism of the chain propagation step.

In terms of the theory, vibrationally excited hot radicals are formed in the propagation step, and these radicals have, at the moment of their formation, surplus energy originating from the reaction heat and the activation energy of the exothermal propagation step. A kinetic effect can be observed if the lifetime of hot radicals is sufficiently long to undergo reaction with the monomer molecules. Accordingly, there can be two types of propagation steps: the propagation of cool radicals,



and the propagation of hot radicals ( $R^*$ ),



The hot radicals formed can be deactivated upon collision with monomer ( $M$ ) and solvent ( $S$ ) molecules:



In terms of the hot radical theory, the following expression can be derived for the experimentally measurable, so-called effective chain propagation rate constant ( $\bar{k}_2$ ) [13]:

$$\bar{k}_2 = k_2 \left( 1 + \frac{1}{\gamma + \gamma' \frac{s}{m}} \right) \quad (14)$$

where

$$\gamma = k_7^*/k_2^*; \quad \gamma' = k_7'^*/k_2^* \quad (15)$$

are the two deactivation parameters.

Calculating from the data of Table 4, the value of the propagation rate constant extrapolated to infinite dilution is  $k_2 = 110.6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , and the optimum values

of  $\gamma$  and  $\gamma'$  obtained by iteration with the Simplex method are  $\gamma = 1.39$  and  $\gamma' = 12.99$ .

The agreement of our experimental values plotted in Fig. 1 (○) with those of  $\bar{k}_p$  calculated by Eq. (13) (full line) indicates that the solvent effect observed in the St-DBPh system can be described in terms of the hot radical theory with very good approximation. In the case of polymerization in solution, the variation of the termination rate constant can be interpreted by the diffusion theory, while the change of the propagation rate constant can be interpreted by the hot radical theory. These theories are complementary (not concurrent) theories [13], and they are suitable for the interpretation of rates of different elementary processes; the hot

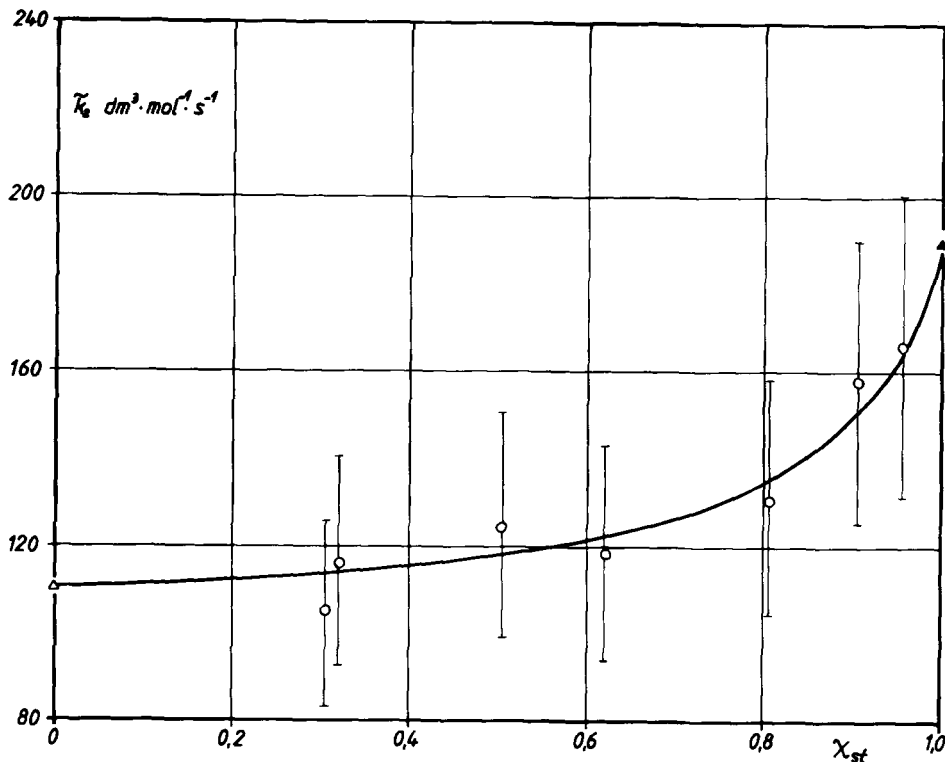


FIG. 1. The propagation rate constant of the polymerization system St-DBPh-50°C plotted against the mole fraction of the monomer. (○) Rotating sector measurements. Full line: in terms of the hot radical theory, (Δ) bulk polymerization value [10], (▲) extrapolated to infinite dilution [10].

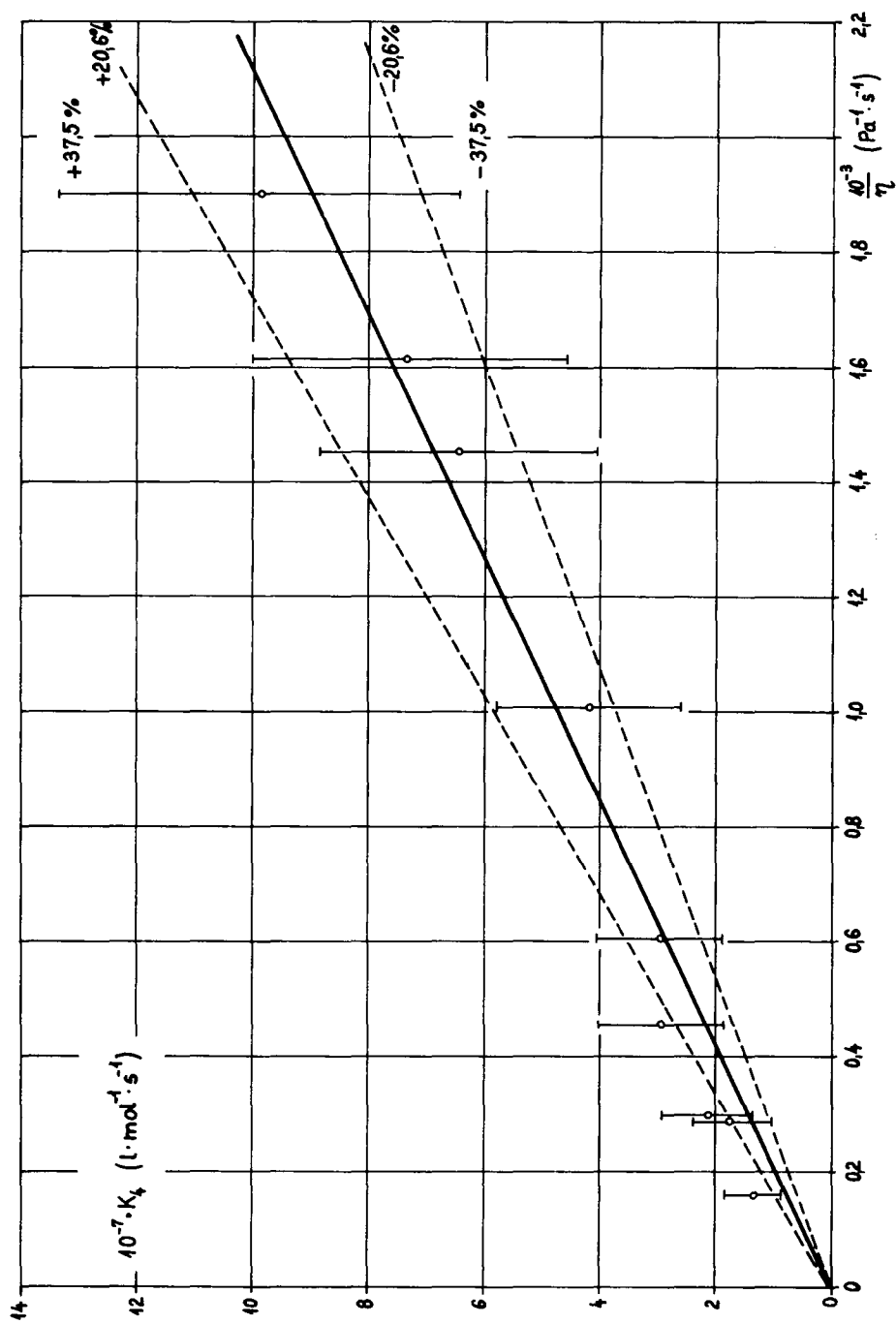


FIG. 2. The dependence of the termination rate constant ( $k_4$ ) on the initial viscosity of the system. (O) Rotating sector measurements.

radical theory for the rate of propagation and the diffusion theory for the rate of termination (Fig. 2).

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