A Thermistor Method for the Determination of Velocity Coefficients of Vinyl Polymerization. V. The Effect of the Bulk Viscosity on the Velocity of Vinyl Polymerization

By Hajime MIYAMA

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Introduction

It is well known that the ratio of the propagation constant to the termination constant k_p/k_t for vinyl polymerization increases with the increase of the degree of conversion[1-4]. Apparently this is a result of the increasing bulk viscosity of the reaction system causing the mobility of monomer M and radical $M_n{}^*$ to slow down. However, no experiment to measure both k_p/k_t and the bulk viscosity η to obtain the relation between these values has been conducted and only M.F. Vaughan's theory[5] for the thermal polymerization of styrene is related to the subject.

The author therefore measured those two values by using a special reaction vessel, which could function as a viscosimeter, compared the results of measurements with the values of k_p and k_t of vinyl acetate given in the 4th paper[1] of this series, and obtained the general formula which gives the relation between η and k_p or k_t.

Theoretical

The theoretical formula, postulated by E. Rabinowitch[6], expresses the effect of the bulk viscosity on the rate constant in the liquid reaction. If liquid can be assumed to possess a quasicrystalline structure, the rate constant c (1.molecule^{-1}.sec^{-1}) for a second-order reaction between two molecules of the same size as the solvent molecules, is

$$c=n\nu\exp(-E/RT)/N_0\,[1+a^2Y\nu\exp(-E/RT)/2D] \qquad (1)$$

where $D=D_A+D_B$, D_A and D_B are the diffusion constants of the two molecules, E is the activation energy, α is the shortest distance between lattice points, n is the co-ordination number of the lattice, ν is the frequency factor, N_0 is the number of lattice points and Y is constant (ca. 2). From this equation Vaughan[5] derived the following approximate formula for the velocity constant k(1 mole.$^{-1}$ sec^{-1}) of the polymerization of styrene.

$$\begin{aligned}k&=\nu\exp(-E/RT)/\\&\quad[1+a^2\nu\exp(-E/RT)/D]\\&=k_0/(1+Q/D)\end{aligned} \qquad (2)$$

where $k_0=\nu\exp(-E/RT)$ and $Q=a^2k_0$.

By the application of this formula to the reaction between monomer M and radical $M_n{}^*$, the propagation process of polymerization was explained and by its application to the reaction between radicals, the termination process was explained. The equation (2) equals, the following equation

$$k_0/k=1+Q/D \qquad (3)$$

If the functional relation between D and η be put as

$$1/D=f(\eta) \qquad (4)$$

then

$$k_0/k=1+Qf(\eta) \qquad (5)$$

Although Vaughan used the Einstein-Stokes' relation as the relation (4), it is doubtful that Einstein-Stokes' relation is applicable for a complex system such as the system of polymerization. Moreover, the validity of the application of the equation (1) seems doubtful because in the propagation and termination process of polymerization, one or both of two reacting molecules is larger in size than the solvent molecules (monomers).

When the reacting molecules are larger than the solvent molecules, the following

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1) H. Miyama, This Bulletin, **29**, 711, 715, 720 (1956); **30**, 10 (1957).

2) W. I. Bengough and H. W. Melville, *Proc. Roy. Soc.*, **A230**, 429 (1955).

3) S. Fujii, This Bulletin, **27**, 216, 238 (1954).

4) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949); **73**, 1700, 5395 (1951).

5) M. F. Vaughan, *Trans. Faraday Soc.*, **48**, 576 (1952).

6) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

relation postulated by M. von Smoluchowski[7] is applicable:

$$
{}_AZ_B = 2\pi (D_A + D_B)(r_A + r_B)N/1000 \\
= 2\pi N(r_A + r_B)D/1000 \qquad (6)
$$

where ${}_AZ_B$ (1.mole^{-1}.sec^{-1}) is the collision number between two molecules A and B, when the concentrations of two molecules are a unit, r_A and r_B are diameters of each molecules and N is Avogadro's number. If it is assumed that only the factor ${}_AZ_B$ of k varies with the variation of the bulk viscosity, then the following relation can be derived

$$
k_0/k = D_0/D = D_0 f(\eta) \qquad (7)
$$

Experimental

By obtaining experimentally the relation between η and k_p/k_t, it is possible to ascertain whether (5) or (7) is applicable for vinyl polymerization. Details of this experiment are as follows:

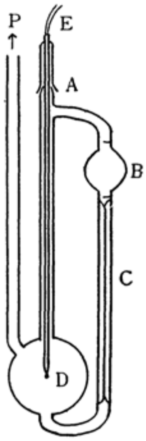

Fig. 1. Reaction vessel.
A; Joint
B, C; Viscosimeter
D; Thermistor
E; Thermistor's lead wires
P; To vacuum

The reaction vessel, shown in Fig. 1, made of soft glass and equipped with a thermistor, is ca. 19 cc. in capacity. Its inside diameter is 40 mm. and the inside depth is 15 mm. This vessel can be connected to the vacuum system at P. The lead wires of the thermistor are covered by very thin soft glass tubing which is sealed at the upper end of joint A. The glass bulb B is ca. 5 cc. in capacity. At its both ends two lines are marked. The capillary C is 10 cm in length and 2.5 mm. in diameter. Using this vessel, the values of k_p/k_t can be measured by the method described in the previous papers[1], and at the same time, the bulk viscosity is obtainable by turning the vessel upside down to transfer the sample into the bulb B, then righting the vessel and measuring the time for the sample to pass between the two marks.

Other experimental procedures and the method of purification of sample and sensitizer are the same as in the previous papers[1]. But the effect of the direct irradiation of light on the thermistor was not observed, because the vessel is made of soft glass and has larger loss in transmission of light than the quartz vessel used in the first paper[1].

Results

The measurement was accomplished on methyl

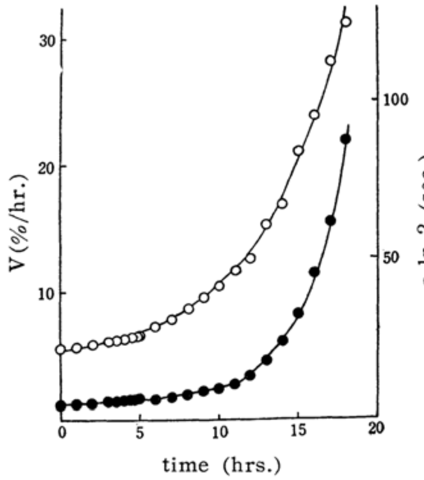

Fig. 2. The variation of rate and lifetime with time for the polymerization of methyl methacrylate.
○ V; ● τ ln 2

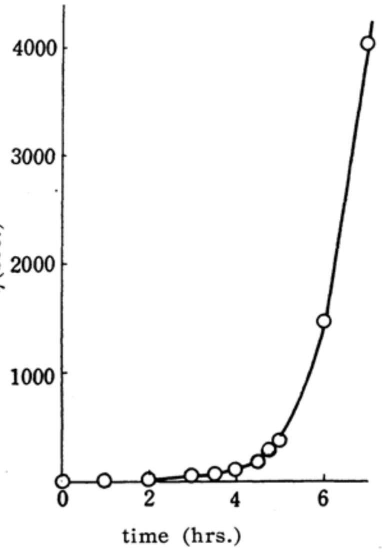

Fig. 3. The variation of bulk viscosity with time for the polymerization of methyl methacrylate.

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[7] M. von Smoluchowski, *Z. Physik. Chem.*, **92**, 129 (1918).

methacrylate and vinyl acetate at 30°C by using 1,1′-azo-biscyclohexanecarbonitrile as a photosensitizer, the concentration of which was 0.013 mole/l in methyl methacrylate and 0.002 mole/l in vinyl acetate.

The variation of the velocity V and the lifetime τ for the polymerization of methyl methacrylate during continuous polymerization are shown in Fig. 2. The variation of the bulk viscosity η (the time measured by viscosimeter) is shown in Fig. 3. By calculating the degree of conversion φ (%) and the values of k_p/k_t as described in the 3rd paper[1] of this series, Table I was obtained.

Table I

The variation of η and k_p/k_t with conversion for the polymerization of methyl methacrylate

Conversion	η(sec.)	$(k_p/k_t)\times10^5$
0	1.3	0.99
0.6	4.1	1.01
1.1	11.5	1.12
1.7	33.0	1.23
2.0	53.8	1.30
2.3	99.4	1.38
2.7	185.1	1.40
2.8	286.5	1.48
3.0	365.2	1.54
3.7	1456.1	1.80
4.4	4030.0	2.22
5.2		2.60
6.2		3.34
7.2		4.04
8.2		5.22
9.4		7.21
10.8		12.1
12.4		18.1
14.3		32.0
16.6		53.6
19.2		85.5
22.1		121.0

The value of k_p/k_t over 22% conversion was not obtainable, because the lifetime was very long and the measurement was impossible. As shown in this table, the increase of k_p/k_t with the degree of conversion is more remarkable than those for other monomers. This result coincides with the results obtained by other methods[3,4]. The increase in the bulk viscosity is more remarkable than the increase of k_p/k_t, but the measurement of the viscosity over conversion 4.4% was impossible, because it took a long time and was not reproducible.

Because details of measurements on the vinyl acetate have already been described in the third paper[1], these are omitted and only their results are shown in Table 2. The measurement of the viscosity over 16.1% was impossible.

Table II

The variation of η and k_p/k_t with conversion for the polymerization of vinyl acetate

Conversion(%)	η(sec.)	$(k_p/k_t)\times10^5$
0	1.0	1.20
1.2	1.4	1.22
2.4	2.1	1.26
3.6	7.5	1.31
4.9	16.9	1.37
6.2	32.7	1.43
7.5	65.0	1.49
8.9	116.5	1.53
10.3	183.1	1.56
10.7	343.5	1.64
13.1	707.7	1.72
14.6	976.1	1.88
16.1	1734.0	2.10
20.8		2.63
28.8		3.50
37.3		4.89
45.5		6.15
53.2		11.0
60.0		18.2
68.1		35.8

Discussion

Let the ratio of the viscosity η at any conversion to η_o at 0 conversion and the same ratio of k_p/k_t be x and y respectively, i. e.

$$\left.\begin{aligned} x&=\eta/\eta_o \\ y&=(k_p/k_t)/(k_p/k_t)_o \end{aligned}\right\} \tag{8}$$

Although the measurement of the viscosity was impossible at high conversion, the following relations were observed between

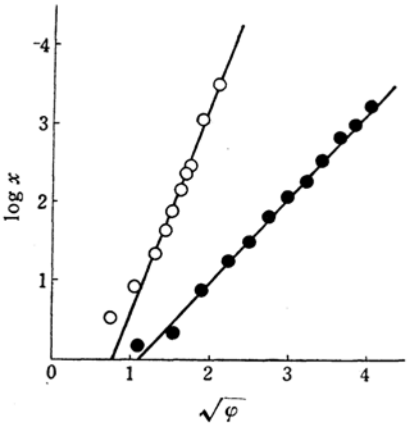

Fig. 4. The variation of $x=\eta/\eta_0$, with conversion φ.
○ Methyl Methacrylate
● Vinyl Hatate

x and φ at low conversion of polymerization as shown in Fig. 4, i. e. on methyl methacrylate,

$$\log x = 2.68\sqrt{\varphi} - 2.17 \tag{9}$$

and on vinyl acetate

$$\log x = 1.11\sqrt{\varphi} - 1.22 \tag{10}$$

These relations are in good agreement with the relation suggested by R. S. Spencer and J. L. Williams[8], in which the bulk viscosity is proportional to $\exp\sqrt{W}$, where W is the weight fraction of polymer. Then the values of the bulk viscosity at high conversion, though not measurable, can be calculated by using (9) and (10). In Table 3, the values of x and y are tabulated.

TABLE III

THE VALUES OF x AND y FOR THE POLYMERIZATION OF METHYL METHACRYLATE AND VINYL ACETATE

Methyl Methacrylate		Vinyl Acetate	
$x^{a)}$	y	$x^{a)}$	y
1.0	1.00	1.0	1.00
3.2	1.02	1.4	1.02
8.3	1.13	2.1	1.05
25.4	1.24	7.5	1.09
41.4	1.31	16.9	1.14
76.3	1.39	32.7	1.19
142.8	1.41	65.0	1.24
221.0	1.49	116.5	1.28
281.5	1.56	183.1	1.30
1121.0	1.82	343.5	1.37
3100.0	2.24	707.7	1.44
$10^{3.96}$	2.62	976.1	1.57
$10^{4.50}$	3.37	1734.0	1.75
$10^{4.92}$	4.08	$10^{4.05}$	2.19
$10^{5.81}$	5.27	$10^{4.74}$	2.92
$10^{6.05}$	7.29	$10^{5.57}$	4.07
$10^{6.68}$	12.2	$10^{6.28}$	5.12
$10^{7.28}$	18.3	$10^{6.90}$	9.17
$10^{8.00}$	32.4	$10^{7.42}$	15.2
$10^{8.72}$	54.2	$10^{7.94}$	29.2
$10^{9.61}$	86.5		
$10^{10.45}$	122.2		

a) In this Table exponential figures are calculated by equations (9) or (10).

Because k_p is constant at the initial stage (until $\varphi = 30-40\%$) of polymerization and the increase of k_p/k_t with the degree of conversion depends mainly upon the decrease of k_t[1-4], y in equation (8) at this stage equals to $(k_t)_0/k_t$, i. e.,

$$y = (k_t)_0/k_t \tag{11}$$

As shown in Figs. 5 and 6, the following relations at the initial stage of polymerization, for methyl methacrylate may be derived:

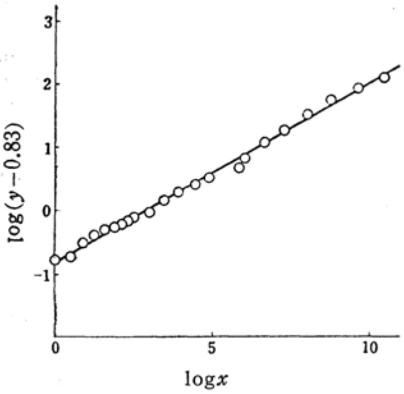

Fig. 5. The variation of y with x for the polymerization of methyl methacrylate.

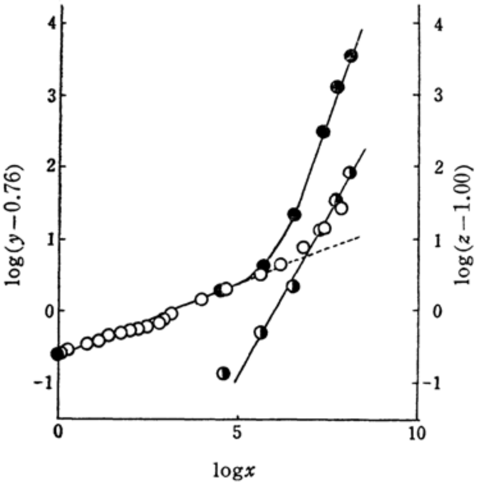

Fig. 6. The variation of y and z with x for the polymerization of vinyl acetate.

○, $y = (k_p/k_t)/(k_p/k_t)_0$;

●, $y = (k_t)_0/k_t$

◑, $z = (k_p)_0/k_p$

$$y = 0.83 + 0.17x^{0.28} \tag{12}$$

and for vinyl acetate

$$y = 0.76 + 0.24x^{0.20} \tag{13}$$

Because k_t is not constant at the later stage of polymerization and $(k_t)_0/k_t$ is not equal to $(k_p/k_t)/(k_p/k_t)_0$, it is necessary to consider k_p and k_t separately. Using the values of the viscosity in this report, it is possible to obtain the relation between the bulk viscosity and k_p or k_t, which was presented on vinyl acetate in the 3rd paper[1] of this series. Since these values

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[8] R. S. Spencer and J. L. Williams, *J. Colloid Sci.*, **2**, 117 (1947).

of k_p and k_t were measured at 20°C, these were corrected to 30°C by using the values of the activation energies E_p and E_t given in the 4th paper¹⁾. Although the variation of y with x at the initial stage obeys the equation (13) as shown in Fig. 6, it is replaced by the relation $y \propto x^{1.5}$ at the later stage. The following equation therefore is applicable throughout the total process of polymerization.

$$y = 0.76 + 0.24(x^{0.20} + 10^{-8}x^{1.50}) \qquad (14)$$

Let the ratio of $(k\ )_0$ to $k_,$ be z, i. e.

$$z = (k_p)_0/k_p \qquad (15)$$

Then the following equation is obtainable from Fig. 6 throughout the total process of polymerization,

$$z = 1 + 0.65 \times 10^{-6}x \qquad (16)$$

As shown in Table IV, there is a good agreement between the calculated values of y or z by using equation (14) or (16) and the experimental values.

TABLE IV

THE COMPARISON OF CALCULATED VALUES WITH EXPERIMENTAL VALUES ON y AND z FOR THE POLYMERIZATION OF VINYL ACETATE

Conversion (%)	x	y(exp.)	y(calc.)	z (exp.)	z (calc.)
0	1	1.00	1.00	1.00	1.00
28.15	$10^{4.68}$	2.64	2.85	1.14	1.03
39.00	$10^{5.71}$	4.82	4.33	1.50	1.33
49.80	$10^{6.61}$	23.8	26.2	3.38	3.64
59.30	$10^{7.33}$	337	248	14.9	14.9
66.40	$10^{7.73}$	1250	966	35.5	35.9
71.10	$10^{8.15}$	3780	3991	91.8	92.8

From the comparison of (14) with (7), the following equation is obtained:

$$(k_t)_0/k_t = (D_R)_0/D_R = 0.76 + 0.24(x^{0.20} + 10^{-8}x^{1.50}) \qquad (17)$$

And from the comparison of (16) with (7)⁹⁾,

$$(k_p)_0/k_p = (D_M)_0/D_M = 1 + 0.65 \times 10^{-6}x \qquad (18)$$

where D_M and D_R are the diffusion constants of monomer M and radical $M_n{}^*$ respectively. There is no direct measurement of the diffusion constant of monomer, but Melville et al.²⁾ estimated its value by measuring the diffusion velocity of α,α'-diphenylpicrylhydrazil in the various conversions of vinyl acetate. Comparison of these values of $(D_M)_0/D_M$ with the values of η/η_0 of this report is shown in Fig. 7. Here it is apparent that the measured values of $(D_M)_0/D_M$ obey the relation (18). This result shows that the application of (7) is reasonable. At the same time, the relation (17) is shown in Fig. 7 and the shape of this curve is similiar to the curve (18), except that $(D_R)_0/D_R$ increases with the increase in the bulk viscosity at rather low viscosity. It seems probable that the effect of the bulk viscosity is more remarkable on the diffusion constant of the radical than on that of the monomer.

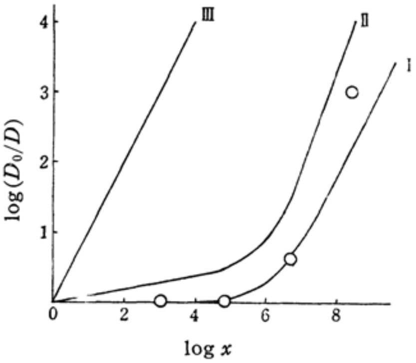

Fig. 7. The variation of D_0/D with x
I, $D_0/D = 1 + 0.65 \times 10^{-6}x$;
II, $D_0/D = 0.76 + 0.24(x^{0.20} + 10^{-8}x^{1.50})$:
III, $D_0/D = x$;
○, The measured values of D_0/D

If the Einstein-stoke's relation adopted by Vaughan is applicable, $(D_M)_0/D_M$ may be expressed in a different form from (18), i.e.

$$(D_M)_0/D_M = x \qquad (19)$$

The measured values of $(D_M)_0/D_M$ deviate greatly from this relation. On the other hand, if $a \fallingdotseq 3 \times 10^{-8}$cm.⁶⁾, $k_0 \fallingdotseq 5 \times 10^2$ ¹⁾ and $D_0 \fallingdotseq 10^{-5}$ cm².sec⁻¹ ⁵⁾ are used in the Vaughan's equation (3), the values of Q becomes ca. 5×10^{-13} and from the comparison of (3) with (16), $(D_M)_0/D_M$ equals ca. 10^2x.

$$(D_M)_0/D_M = 10^2x \qquad (20)$$

This result (20) is more unsatisfactory than the equation (19) for the measured values of $(D_M)_0/D_M$. Therefore the application of (5), (3) and (1) is not considered reasonable. The reason why Vaughan's qualitative application of the equation (1) for the polymerization of styrene gave apparently valid results may be his rather arbitrary selection of the values of the diffusion constants and the

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9) Although $D = D_M + D_R$ in the propagation process, it seems reasonable to assume $D = D_M$ because $D_M \gg D_R$.

use of an assumed relation $1/D \propto \eta$.

From the above discussion, it seems that the application of (7) and (6) is more reasonable than (5) and (1) for the propagation and termination process of polymerization, in which the reacting molecules are far larger than the solvent molecules. But to prove this conclusion absolutely, it is necessary to measure the bulk viscosity at high conversion and the diffusion constants of monomer and radicals, though they are not measurable in this study.

Summary

The author measured the ratio of the propagation constant to the termination constant k/k_t and the bulk viscosity η of the reaction system for the polymerization of methyl methacrylate and vinyl acetate by using the thermistor method and a special reaction vessel, which could be used as a viscosimeter, then compared the results of these measurements with the values k_p and k_t of vinyl acetate presented in the previous paper[1], and thus obtained the general formula for the relation between the bulk viscosity and k_p or k. The obtained results are summarized as follows;

1) Throughout the total procss for the polymerization of vinyl acetate the relation between the termination constant k_t and η is expressed as follows,

$$(k_t)_0/k_t=0.76+0.24[(\eta/\eta_0)^{0.20}+10^{-8}(\eta/\eta_0)^{1.50}]$$

In case of methyl methacrylate, the following formula is recommended which holds up to 22% conversion.

$$(k_t)_0/k=0.83+0.17(\eta/\eta_0)^{0.28}$$

Where $(k_t)_0$ and η_0 are the values of k_t and η at conversion 0.

2) The propagation constant k, and η in the polymerization of vinyl acetate are expressed as follows.

$$(k_p)_0/k=1+0.65\times10^{-6}(\eta/\eta_0)$$

3) These results can be explained by the assumption that k_t and k_p are proportional to the diffusion constants of reacting molecules. Using the theory of Rabinowitch-Vaughan, we find some difficulties to explain our experimental results.

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Department of Chemistry,
Defense Academy, Yokosuka