A Thermistor Method for the Determination of Velocity Coefficients of Vinyl Polymerization. III

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Introduction

In the previous papers of this series[1] the author described, a thermistor method for the measurement of the rate of vinyl polymerization and obtained the values of k_p/k_t for styrene, vinyl acetate and methyl methacrylate in the initial stages of polymerization. As well as the thermocouple method, this method is not only applicable to the initial stages of polymerization, but can be used equally well for the study of the later stages when the reaction mixture becomes a viscous syrup or solid gel. Recently velocity coefficients for the later stages of the polymerization of vinyl acetate were evaluated by Melville and his co-worker with the use of a thermocouple[2].

In this paper, the author uses the thermistor method for studying the later stages of vinyl acetate polymerization. The monomer was photosensitized by the addition of 1,1'-azobiscyclohexanecarbonitrile, which is a better sensitizer than α-azobisisobutyronitrile, from the points of view of effectiveness and lack of accelaration of polymerization in the dark.

Theoretical

From the kinetics of polymerization[3], the fractional rate of polimerization is represented by equation (1).

$$V=-1/M.\ \ \mathrm{d}M/\mathrm{d}t=k_p(V_{init}/k_t)^{1/2} \tag{1}$$

where k_p, k_t, V_{init}. and M are propagation constant, termination constant, velocity of of initiation and concentration of monomer respectively. Because V_{init}. of this equation is not varied by temperature-change in the photopolymerization, the difference between activation energy of propagation and the one half of activation energy of termination $E_p-1/2E_t$ can be obtained by measuring the variation of the fractional rate V with the temperature.

The lifetime of the active species τ is shown as follows.

$$\tau=(k_p/k_t)\times 1/V \tag{2}$$

From Eqs (1) and (2) the following equation can be obtained.

$$\tau=(k_t\times V_{init})^{-1/2} \tag{3}$$

Since V_{init} is not varied by the temperature-change in the photopolymerization, the activation energy of termination can be obtained by measuring the value τ at various temperatures.

An estimate of the extent of conversion can be obtained by the next formulas. Thus M of Eq. (1) is replaced by the initial concentration of monomer M_0,

$$V_0=-1/M_0\ \ \mathrm{d}M/\mathrm{d}t \tag{4}$$

If the variation of V_0 against time t is measurable, M at any time t can be calculated according to the following equation.

$$M_0-M=M_0\int_{t_0}^{t}V_0\mathrm{d}t \tag{5}$$

where t_0 is the initial time. Thus the extent of conversion φ is expressed as follows.

$$\varphi=(M_0-M)/M_0=\int_{t_0}^{t}V_0\mathrm{d}t \tag{6}$$

Using the thermistor method, the value of V_0 can be obtained when specific heat of the system and heat of polymerization are known, as shown in the previous papers of this series. But the correct values of V_0 at various degrees of conversion are unknown, because the specific heat of the system varies with the extent of conversion. Approximately, the extent of conversion can be obtained by assuming that the specific heat does not change with conversion. Then using the specific heat at these values of conversion, the values of V_0 are corrected and therefore values of ρ are corrected. Repeating these procedures the correct values of V_0 and φ can be, obtained, although the extent of conversion cannot be measured directly and the specific heat of the system varies with the degree of conversion.

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[1] H. Miyama, This Bulletin, **29**, 711 (1956). H. Miyama, ibid., **29**, 715 (1656).

[2] W. I. Bengough and H. W. Melville, *Proc. Roy. Soc.*, **230**, 429 (1955).

[3] C. E. H. Bawn, "The Chemistry of High Polymers", London (1948), p. 68.

Experimental

The experimental apparatus and the preparation of vinyl acetate are the same as described in the previous papers1). 1,1'-azobiscyclohexanecarbonitrile was purified through recrystallization from ethanol and its ultraviolet absorption spectrum is shown in Fig. 1. The variation of the rate of polymerization and that of the lifetime with the intensity of irradiation was usually studied at 20°C. The temperature was then raised as rapidly as possible to other temperatures, and measurements of the rate and of the corresponding lifetime were performed. As soon as the necessary measurements had been done, the thermostat was cooled rapidly to 20°C. The rate and the lifetime at 20°C were then measured and compared with the values obtained before heating. The monomer was then polymerized to a further stage by continuous irradiation using an ultra high pressure mercury lamp. When the next arbitrary stage of the polymerization was attained, irradiation was discontinued and the sequence of measurement of rates and lifetimes was repeated. This procedure was repeated until the rate became so slow and the lifetime so great that accurate determination was impossible. The extent of conversion was obtained from the fractional velocity change with time, using Eq. (6). As specific heat of vinyl acetate, the next value2) was used. (p. 2)

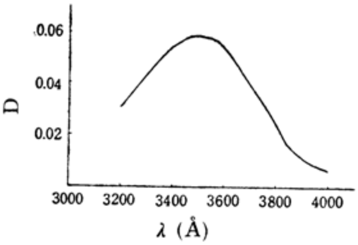

Fig. 1. Ultraviolet absorption spectrum of 0.003 mol./l. 1, 1'-azobiscyclohexanecarbonitrile in vinyl acetate.

$$\text{Specific heat} = 0.470 - 0.081\,\varphi \qquad (7)$$

where φ is the extent of conversion.

Experimental Results

All measurements were carried out by using 0.003 mol./l. 1,1'-azobiscyclohexaecarbonitrile as photosensitizer.

The variation of velocity V_0 during continuous polymerization is shown in Fig. 2. Using Eq. (6), the variation of velocity V_0 with the extent of conversion is shown in Fig. 3. These values of V_0 and φ were corrected using the already described theory and specific heat (7). The first correction is shown by broken curves I in Fig. 2 and 3 and the second correction by broken curves II. In these figures, curves I and II are almost the same. To check these values of conversion the reaction mixture was dissolved in acetone; the polymer was precipitated by addition of methanol and weighted. The comparison is shown in Table I.

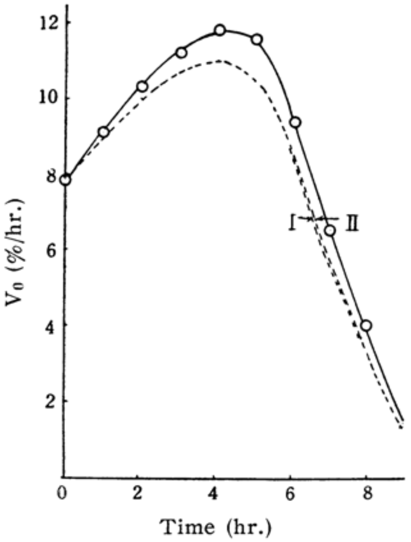

Fig. 2. Variation of the rate V_0 during the continuous polymerization at 20°C.

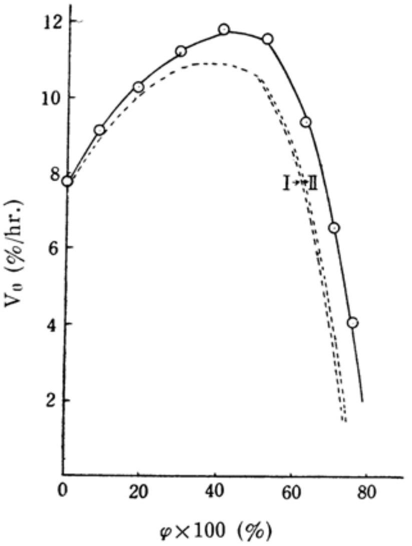

Fig. 3. Variation of the rate V_0 with conversion at 20°C.

TABLE I

COMPARISON OF CALCULATED CONVERSION WITH MEASURED ONE

Uncorr.	1st Corr.	2nd Corr.	Meas.
78.80%	73.60%	73.80%	75.20%

From these results it is seen that the first correction is good enough for use, within the experimental error. Therefore the first corrected values of V_0 and φ will be used hereafter.

The variation of the rate with intensity of irradiation at various stages of the reaction is shown in Fig. 4. From this figure, the exponent is 0.5 until 49.80% conversion. As polymerization proceeds over this conversion, the exponent exceeds 0.5, therefore the theory described in

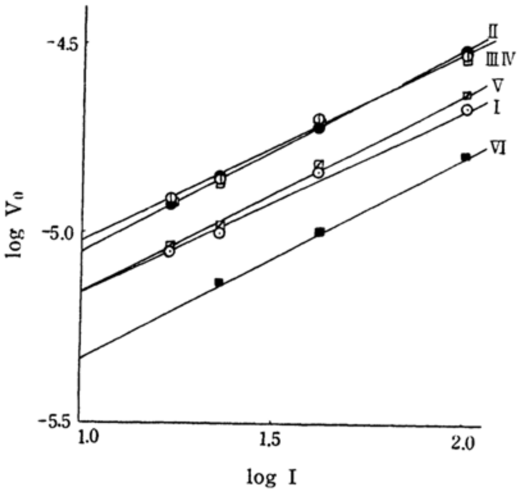

Fig. 4. Variation of the rate with the light intensity at 20°C, where V_0 is expressed in the unit of sec^{-1}.
○ Curve I, at 0% conversion; ⦶ Curve II, at 28.15% conversion; ● Curve III, at 39.00% conversion; □ Curve IV, at 49.80% conversion; ⧄ Curve V, at 59.30% conversion; ■ Curve VI, at 66.40% conversion.

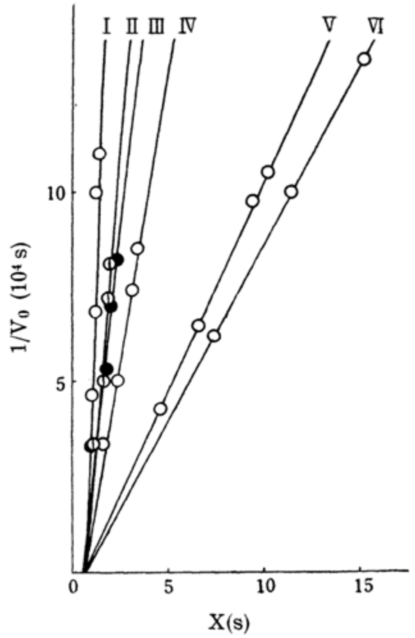

Fig. 5. Variation of the rate V_0 with the measured intercept at 20°C.
○ Curve I, at 0% conversion; ⦶ Curve II, at 28.15% conversion; ● Curve III, at 39.00% conversion; ○ Curve IV, at 49.80% conversion; ○ Curve V, at 59.30% conversion; ○ Curve VI, at 66.43% conversion.

the first paper of this series cannot be applied correctly and the results at later stages are less accurate than those at initial stages.

The variation of the rate with the measured intercept X is shown in Fig. 5. From this intercept, the instrument's lag in response can be obtained and is 0.6−0.9 sec. From the slope of this line the values of k_p/k_t can be calculated. But at the conversion of 71.10%, the linearity between X and $1/V_0$ cannot be seen, because the lifetime becomes greater and velocity becomes slower. The values of V_0 and X at this conversion are shown in Table II.

TABLE II

VARIATION OF RATE AND LIFETIME WITH INTENSITY OF IRRADIATION AT 20°C AND AT 71.10% CONVERSION

Light Intensity	$V_0(s^{-1})$	$X(s)$	k_p/k_t
100	1.00×10^{-5}	14.5	20.0×10^{-5}
46	0.62×10^{-5}	19.7	19.0×10^{-5}
		Average	18.5×10^{-5}

The value of k_p/k_t in Table II is calculated by assuming that instrument's lag in response C in equation $X=C+(k_p/k_t)\times(1/V_0)\times\ln 2$ is 0.7 sec. The k_p/k_t value at various conversions is summarized in Table III.

TABLE III

THE VALUE OF k_p/k_t AT VARIOUS CONVERSION AT 20°C

Conversion (%)	$k_p/k_t\times10^{-5}$
0	1.08
28.15	2.02
39.00	2.72
49.80	4.78
59.30	13.1
66.40	16.3
71.10	18.5

The variation of rate V_0 with the extent of conversion at 30°C and 40°C is shown in Fig. 6.

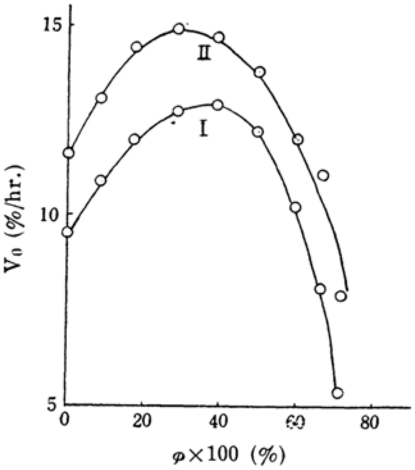

Fig. 6. Variation of the rate V_0 with conversion at 30°C and 40°C.
Curve I, at 30°C; Curve II, at 40°C.

where φ is the first corrected value. At these temperatures, the measurement of rate and life-time at various light intensities was not carried out and the instrument's lag was unknown. But by using the lag at 20°C, the value of the life-time was calculated according to the equation $X=C+\tau \ln 2$. The value of $\tau \ln 2$ at various conversions is shown in Fig. 7. The lifetime does not vary remarkably until 50% conversion is attained, but beyond this point it increases rapidly.

From Figs. 3 and 6 the variation of the rate with temperature can be obtained as shown in Fig. 8. And from Fig. 7 the variation of the lifetime with the temperature can be obtained as shown in Fig. 9.

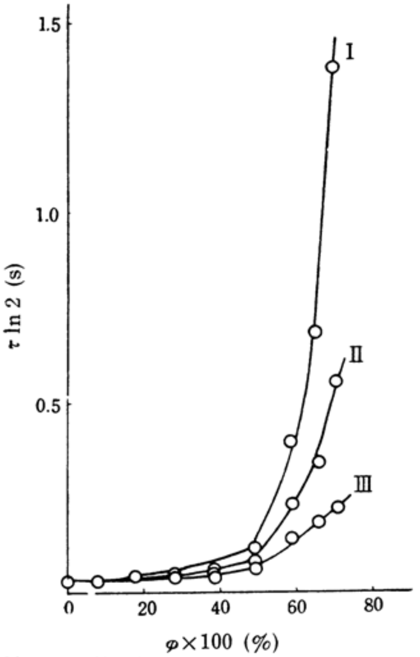

Fig. 7. Variation of the lifetime with conversion.
Curve I, at 20°C; Curve II, at 30°C; Curve III, at 40°C.

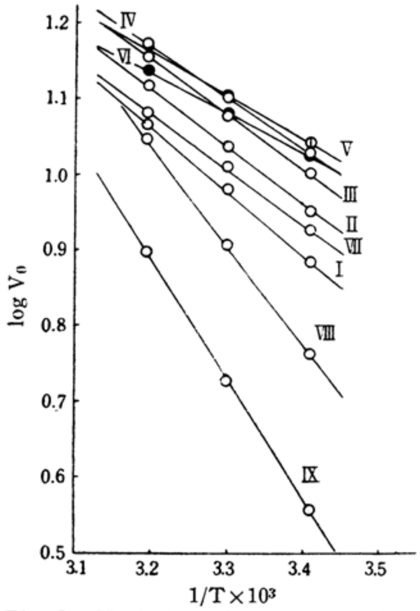

Fig. 8. Variation of the rate with temperature, where V_0 is expressed in the unit of %/hr.
Curve, I, at 0% conversion; Curve II, at 8.3% conversion; Curve III, at 17.8% conversion; Curve IV, at 28.15% conversion; ◐ Curve V, at 39.00% conversion; ● Curve VI, at 49.80% conversion; Curve VII, at 59.30% conversion; Curve VIII, at 66.40% conversion; Curve IX, at 71.10% conversion.

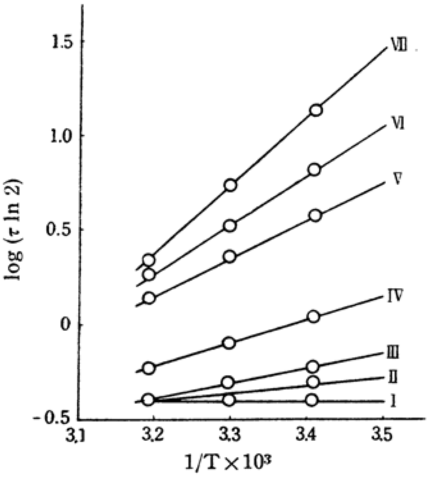

Fig. 9. Variation of the lifetime with temperature.
I, at 17.8% conversion; II, at 28.15% conversion; III, at 39.00% conversion IV, at 49.80% conversion; V, at 59.30% conversion; VI, at 66.40% conversion; VII, at 71.10% conversion.

Discussion

Because the value of k_p/k_t in Table III is calculated by using V_0 of Eq. (4), it is necessary to correct these values by using the true fractional rate V. From Eqs. (1) and (4) V can be expressed as follows.

$$V=V_0\times(M_0/M)=V_0/(1-\varphi) \qquad (8)$$

Since $k_p/k_t=V\times\tau$, the true k_p/k_t values can be obtained through multiplication $1/(1-\varphi)$ by the values of Table III. These values are summarized in Table IV, comparing with Melville's results[2]).
From both the results it is clear that the value of k_a/k_t increases gradually until 50% conversion and beyond this point increases rapidly. But the author's values are lower than the values obtained by Melville.

The overall activation energy $E_p-\frac{1}{2}E_t$ and activation energy of termination E_t are obtained from figures 7 and 8 and compared with Melville's values[2] in Table V.

TABLE IV

THE CORRECTED VALUE OF k_p/k_t COMPARED WITH MELVILLE'S VALUE AT VARIOUS CONVERSIONS

Conversion	$k_p/k_t\times10^5$	
%	This Work[a]	Thermocouple Method[b]
0	1.08	
4		3.72
23		10.2
28.15	2.82	
39.00	4.13	
46		22.1
49.80	9.55	
57		82.8
59.30	32.3	
65		75
66.40	48.6	
71.10	64.2	

a) This measurement was carried out at 20°C.
b) This measurement was carried out at 25°C.

TABLE V

THE VALUE OF $E_p-1/2\ E_t$, E_t AND E_p AT VARIOUS CONVERSIONS, COMPARED WITH MELVILLE'S VALUE

Conversion	$E_p-\frac{1}{2}E_t$ (kcal./mol.)		E_t (kcal./mol.)		E_p (kcal./mol.)	
(%)	This Work	Melville	This Work	Melville	This Work	Melville
0	3.7		0		3.7	
4		4.2		<1		≥4.2
6		4.2		<1		≥4.2
8.3	3.4		0		3.4	
17.8	3.4		0		3.4	
20		4.0		—		≥4.0
23		3.5		1.4		4.2
28.15	2.8		2.2		3.9	
39.00	2.6		3.8		4.5	
46		1.9		3.4		3.6
49.80	2.5		5.6		5.3	
54		2.0		10.8		7.4
57		2.7		11.8		8.6
59.30	3.3		9.4		8.0	
65		>4.9		>13.0		>11.4
66.40	6.0		12.2		12.1	
71.10	7.2		16.8		15.6	
73		>6.7		>15.4		>14.4

Where E_p is calculated from $E_p-1/2\ E_t$ and E_t. In both values, the overall energy of activation remains constant up to 20% conversion and then gradually decreases to a minimum value in the region of 50% conversion. It then increases rapidly beyond this region. The activation energy of termination is very low at the initial stages but it gradually increases at 20−30% conversion and then increases through the polymerization. On the other hand, the activation energy of propagation remains constant until 40−50% is reached and then increases very rapidly as further polymerization takes place.

Although differences between the author's and Melville's values are, to some extent, observed in Tables IV and V, the qualitative tendency coincides satisfactorily in spite of the differences of methods and temperature.

From these results, it seems that as the polymerization proceeds, increasing viscosity effects the termination process to slow down, but the effect of viscosity upon the propagation process is not so marked and becomes appreciable only at high conversions. But this conclusion must be proved by further study and in the next paper the author will describe the variation of k_p and k_t with the extent of polymerization.

Summary

The author used a thermistor method to study the later stages of polymerization of vinyl acetate, which was photosensitized with 1,1'-azobiscyclohexanecarbonitrile and obtained the variation of k_p/k_t, E_p and E_t with conversion.

From these results it was observed that the value of k_p/k_t increases gradually until about 50% conversion is reached and beyond this point increases rapidly. At the same time, the extent of conversion effects E_t in the region of 20−30% conversion, but the effect upon E_p is not so marked in these stages and becomes appreciable at high conversions.

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