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

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Introduction

Various methods have been described for the measurement of the rate of vinyl polymerization. Dielectric constant[1] and refractive index[2] methods are suitable to follow rapidly the rate of exothermic polymerization in liquid-phase since these methods are sensitive to the slight rise in temperature during the reaction. However, these methods are applicable only with difficulty, therefore it is desirable to measure the small temperature rise with an easier operation. Thus recently the thermocouple method[3] was investigated by H. W. Melville et al. for the measurement of the rate of vinyl porymerization. Instead of using a thermocouple, the author used a bridge consisting of two thermistors, one of which was equipped at the center of a reaction vessel and the other was placed at the center of a standard vessel, to obtain better results from the point of view of sensitivity in temperature, adiabatic period of the system, response time of the instrument and saving the space of the reaction vessel.

This paper is concerned with the measurement of the ratio of the propagation constant to the termination constant for styrene polymerization which is catalyzed by 2, 2′-azobispropane. The data are compared with the values obtained by other methods.

Theoretical

Since the theory of this work is the same as that used in Melville's thermocouple method, the author describes briefly the outline of the theory. When the reaction vessel, which contains monomer M, is irradiated and photopolymerization takes place, the relationship between time t and fractional conversion $\Delta M/M$, is shown as follows.

$$\Delta M/M = k_p/k_t \ln \cosh (t/\tau) \tag{1}$$

where k_p and k_t are the propagation and termination rate constants respectively and τ is the lifetime of the active species before they are removed by mutual termination. When t exceeds 3τ this relation becomes approximately linear.

$$\Delta M/M = k_p/k_t (t/\tau - \ln 2) \tag{2}$$

The values of $\tau \ln 2$ and $k_p/k_t \times 1/\tau$ can be obtained from the interception of the time axis and the slope of this straight line. While the reaction remains adiabatic, the rise in temperature is directly proportional to the fractional conversion. Thus, provided that the heat of polymerization and the heat capacity of the system are known, the accurate values of k_p/k_t and τ can be obtained. Because of the lag in response of the instrument itself, however, the intercept does not represent τ ln 2, but the measured intercept X is given by

$$X = C + \tau \ln 2 \tag{3}$$

where C is the lag in response of the instrument. From the kinetics of polymerization, the following formula can be obtained

$$\tau = k_p/k_t \times 1/V \tag{4}$$

where V is the fractional rate of polymerization. From Eqs. (3) and (4)

$$X = C + k_p/k_t \times 1/\mathrm{V} \times \ln 2 \tag{5}$$

Hence the plot of the measured interception X aginst the reciprocal of the rate $1/V$ is a straight line. The value of k_p/k_t depends only upon the slope of the line and therefore is independent of the response lag of the instrument, when this is of the same order with or less than the lifetime. But to use the theory described above, it is necessary to plot the logarithm of the light intensity $\log I$ against the logarithm of the fractional rate $\log V$ and to verify that the intensity exponent is 0.5 in this plot, as poved by Melville[3].

Experimental

The reaction vessel, shown in Fig. 1, made of transparent quartz and equipped with a thermistor is ca. 9 cc. in capacity. Its inside diameter is 38 mm., inside depth is 8 mm. and this vessel can be connected to the vacuum system by the softglass-quartz joint A. B and C are both softglass-quartz joints. This vessel can be cleaned easily after the reaction by removing the joints B and

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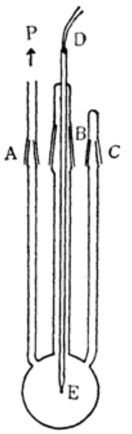
[1] C. M. Burnell, T. G. Majury and H. W. Melville, *Proc. Roy. Soc. London*, **A 205**, 309 (1951); T. G. Majury and Melville, ibid., **A 205**, 323 (1951).

[2] N. grassie and H. W. Melville, ibid., **A 207**, 285 (1951).

[3] W. I. Bengough and H. W. Melville, ibid., 225, 331 (1954).



A, B, C; Softglass-quartz joints
D; Thermistor's lead wires
E; Thermistor
P; To vacuum

Fig. 1. Reaction vessel.

C. The lead-wires of thermistor are covered by very thin softglass tube which is sealed at the upper end of the joint B and the thermistor is placed at the center of the reaction vessel. One of such reaction vessels is used as a standard of temperature. Each thermistor, made by Ohizumi Factory, has the same characteristics shown in Fig. 2, of the temperature-resistance relation.

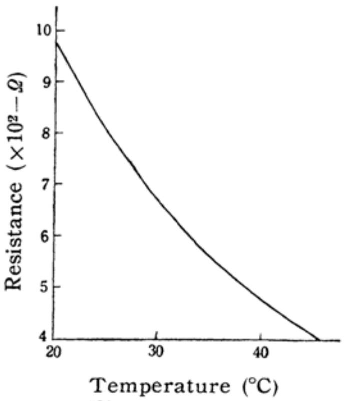


Fig. 2. Thermistor's charactestics.

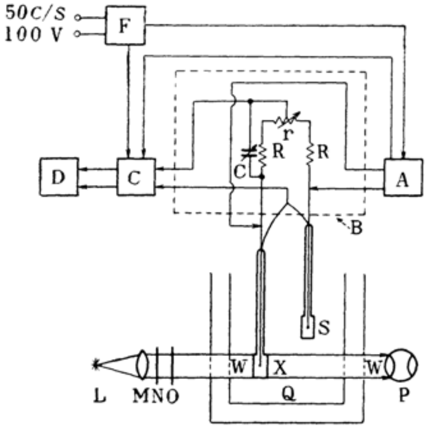


Fig. 3. Diagram of arrangement.
A ; 700 c/s Oscillator B ; Bridge
C ; 700 c/s Amplifier
D ; Penwriting-Oscillograph
F ; Regulated power supply
L ; Light-source M ; Quartz lense
N ; Shutter O ; Filter
P ; Photo-cell
Q ; Double-thermostat W ; Quatz-windows
X, S ; Thermistors

A diagram of arrangement is shown in Fig. 3. In this figure, the oscillator A supplies the constant voltage 700 c/s sine waves to the bridge B and at the same time it is connected to the phase-discriminator of the amplifier C for detecting plus or minus sign of temperature difference. The bridge consists of two identical thermistors, X and S, two equally valuable resistance R, a variable resistance r and a variable condensor c. When two thermistors X and S are situated at the same temperature, the bridge can be balanced by varying the value or r and c. Then, if the temperature of S does not change but that of X changes, the balance of the bridge is broken up and the bridge supplies the output voltage e to the amplifier c. By a simple calculation, e is represented as follows.

$$e=(\Delta r/4r_0)E \tag{6}$$

where E is the input voltage to the bridge, r_0 is the resistance value of thermistors and Δr is a resistance-change of one thermistor caused by the temperature change. When $E=2.0$ V is used $e=20\,\mu$V. for the temperature change of 0.001°C, provided that the resistance-change is ca. 4% for the temperature change of 1°C as shown in Fig. 2. The degree of amplification can be controlled from 1 to 1000 by gain-controller and multiplier of the amplifier. As to the amplifier, frequency is 700 c/s, gain is ca. 110 db and noise is ca. 1.5 μV. expressed in the same unit of the input signal. Therefore noise is neglegible for the temperature change of 0.001°C. The output from the amplifier is displayed on the galvanometer, the direct current resistance of which is 8 kΩ and amplitude per current is 15 mm./mA, of the pen-writing oscillograph D. Velocity of recording-paper can be varied in ten steps from 120 mm./sec. to 5 mm./min. The regulated power supply F is constructed so as to eliminate the outer noise and to stabilize the filament- and B-Voltage of the oscillator and the amplifier.

The source of light is a 400 watt high pressure mercury lamp (Japan Storage Battery Co. Type HL-400) fed from a constant voltage transformer. The light is passed through a quartz lens and then a Matsuda UVD$_1$ filter to obtain parallel and monochromatic (3660 Å) light. During the experiment the constancy of light is checked by a photocell 931 A.

Two vessels with thermistors are placed in a double water thermostat equipped with quartz-windows, which is regulated to ±0.001°C.

Commercial styrene is purified and distilled into the reaction vessel according to the method of Fujii[4].

2, 2′-Azobispropane was prepared by M. Shinichi Taira of Tokyo Metropolitan University and

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[4] Saburō Fujii, This Bulletin, 27, 216 (1954).

was used after distillation, b.p. 88.5°C, n_D^{23} 1.3890. In Fig. 4 is shown its absorption spectrum.

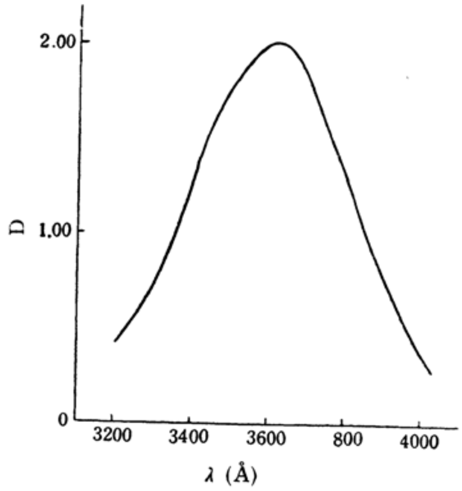

Fig. 4. Absorption spectrum of 2, 2′-azobispropane at the concentration of 0.099 Mol./L in styrene.
D ; Optical density measured by Hitachi spectrophotometer EPB-U

The experimental procedure is as follows. The outputs of two thermistors are balanced by using a variable condensor c and resistance r of the bridge. A light through a lens and a filter UVD_1, irradiates the reaction vessel. At the same time, the time-mark is written on the recoreing-paper by an electric switch. After the reaction proceeds in a measurable amount, the shutter is closed and the time-mark of cutting-off light is recorded. The degree of amplification is adjusted so that the curve on the recording paper can be analyzed. This procedure is repeated until the results are reproducible.

Results

As a blank test, the reaction vessel which contained air or benzene but not monomer, was irradiated by light through a UVD_1 filter. The temperature-rise of the order of 10^{-3}°C was observed and this was supposed to be caused by the direct irradiation on the thermistor. Therfore a center of the outer surface of the reaction vessel was covered by a white-paint spot of ca. 5 mm. diameter to eliminate this effect by shutting out the direct irradiation on the thermistor. Then no temperature-rise was observed.

One of the curves of the recording-paper is shown in Fig. 5, in which A and B are the marks of opening shutting the and shutter respectively. This measurement was performed at 30°C, using 0.0202 mol./l. of 2, 2′-azobispropane. Another vessel, used as a standard, was filled with benzene. Even if monomer and sensitizer were placed in that vessel as well as in the reaction vessel, the curve was the same as that when only benzene was used. This means that the dark reaction is neglegible within the experimental error, compared with the light reaction. Accordingly all measurements were carried out under the condition that the standard cell was filled with benzene.

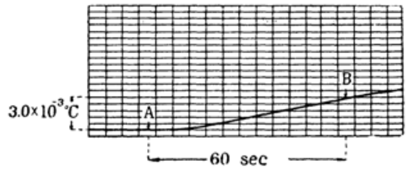

Fig. 5. A recorder trace of a typical experiment for the polymerization of styrene sensitized by 2, 2′-azobispropane.

According to the theory equation (2) is true when t exceeds 3τ, but many measurements showed that this equation could be used when t exceeds approximately 1.5τ.

The necessary constants of styrene at 30°C are as follows[5].

Heat capacity	43.9 cal./mol.
Heat of polymerization	16.76 kcal./mol.

Therefore the relation between the conversion of monomer and the temperature-rise is

$$1\% = 3.82°C \tag{7}$$

The relation between the temperature-rise of the reaction vessel and the amplitude of the oscillograph was checked experimentally at various temperature differences. The resistance-temperature curve of the thermistor as shown in Fig. 2 is not correctly lineart and therefore the amplitude-temperature-rise relation is not the same at different temperature-rise relation is not the same at different

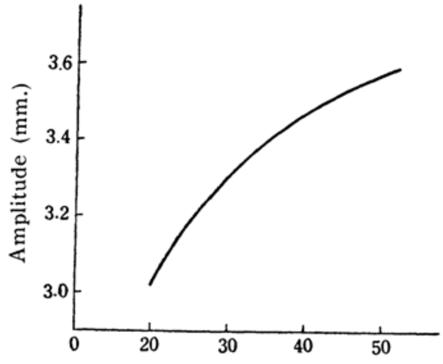

Fig. 6. The amplitude corresponding to the temperature difference of 0.001°C at maximum sensitivity.

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[5] Ray H. Boundy and Raymond F. Boyer, "Styrene", Reinhold, New York (1952), pp. 67, 68.

temperatures. Provided that the amplification is at its maximum sensitivity, the amplitude necessary to detect the temperature difference of 0.001°C is shown in Fig. 6. Therefore at 30°C, the amplitude of the recording paper is shown as follows.

$$1\ \text{mm.} = 3.0\times10^{-4}\,^{\circ}\text{C} \qquad (8)$$

Since the amplitude can be read easily within the accuracy of 0.2 mm. on the recording paper, the sensitivity in temperature is 0.6×10^{-4}C. From Eqs. (7) and (8), the following relation can be obtained.

$$1\ \text{mm/s} = 0.785\times10^{-4}\%/\text{s} = 0.785\times10^{-6}/\text{s} \qquad (9)$$

To check this relation, the velocity measured by thermistor method was compared with the one measured dilatometrically. A dilatometer shown in Fig. 7, which was made from transparent quartz and of the same size as the reaction vessel shown in Fig. 1, was used. Under the same conditions, the values measured by the thermistor agreed with the one measured dilatometrically within the error of ±2%. Accordingly the value measured by thermistor method will be used without checking hereafter.

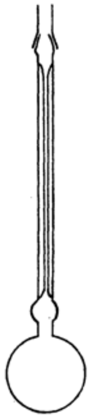

Fig. 7. Dilatometer.

Various filters, of which the transparency factor is known, were used to change the light-intensity.

In Fig. 8 the relation between log *I* and log *V* is shown. From this line's slope, it can be shown that the exponent is 0.5 and therefore the theory already described is applicable.

The relation between $1/V$ and X is shown in Fig. 9. In Fig. 8 and Fig. 9, marks × and ○ are points obtained by using 0.0202 mol./l. and 0.0101 mol./l. of sensitizer respectively.

From the straight line's intercept in Fig. 9, it can be seen that instrument's lag in response is ca. 0.6 sec. This lag is possibly the thermistor's, because the maker of the thermistors gives ca. 0.5 sec. as the lag in response.

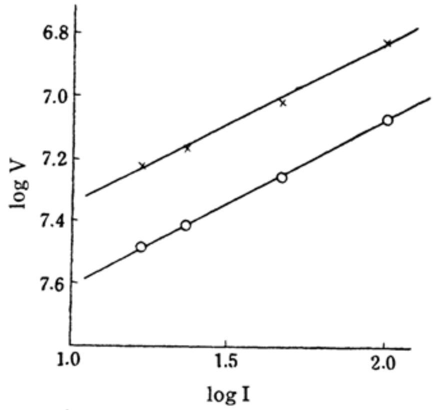

Fig. 8. The relation between log I and log V.

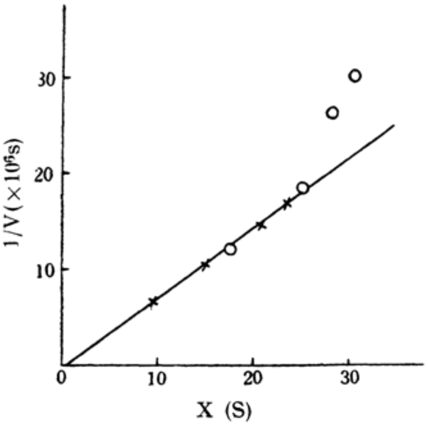

Fig. 9. The relation between X and 1/V.

The time period in which the reaction system remains adiabatic is about 70 sec., from the results of many measurements. One of these result is shown in Fig. 10. Beyond this period, the curve deviates from the straight line. As Melville showed experi-

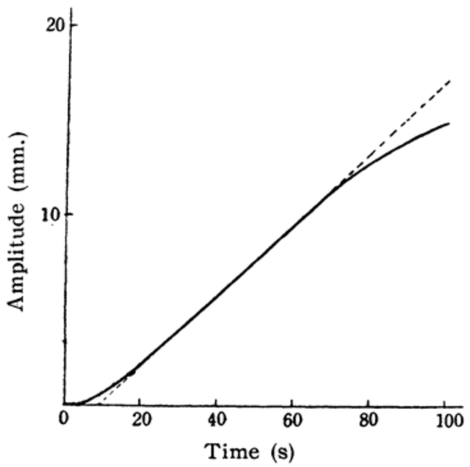

Fig. 10. Deviation of a recorcler trace from the straight line.

mentally the reaction, in which the lifetime is smaller than ca. 1/3 of this period, can be completely analyzed by using his theory. And Fig. 10 shows that the measurements, in which the lifetime is smaller than 25 sec., are all acceptable.

From the slope of Fig. 10, the value of k_p/k_t of styrene at 30°C is 2.02×10^{-6}.

Discussion

Compared with the thermocouple method, the results obtained are better in the points of sensitivity in temperature, adiabatic period of the system and instrument's lag in response. They are shown in Table I compared with the thermocouple method.

TABLE I

THE COMPARISON OF THIS METHOD WITH THE THERMOCOUPLE METHOD

	This method	Thermocouple method
Sensitivity in temperature	0.6×10^{-4}°C	2×10^{-4}°C
Adiabatic time period	70 sec. (9 cc. vessel)	60 sec. (15 cc. vessel)
Instrument's lag in response	0.6 sec.	1–3 sec.

The k_p/k_t value of styrene does not depend upon the concentration of sensitizer used. This value is reasonable in comparison with others obtained by a different method6).

Summary

To measure the rate of vinyl polymerization, a thermistor method was devised and better results were obtained compared with the thermocouple method, in the points of sensitivity of temperature, adiabatic time period, instrument's lag in response and saving the space of the reaction vessel. The k_p/k_t value of styrene at 30°C obtained by this method was 2.02×10^{-6} and reasonable in comparison with other values obtained by different methods.

The auther wishes to express his hearty thanks to Dr. Momotato Suzuki of this Academy for his helpful advice and encouragement and to Mr. Shinichi Taira of Tokyo Metropolitan University for his kind proparation of 2, 2′-azobispropane.

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6) Other values are summarized in ref. 2).